into, and be adsorbed or absorbed therewithin. The silicone resin treated product is typically a rubberized web, or fabric, that is very heavily impregnated with silicone. Such a treated web is substantially devoid of its original tactile and visual properties, and instead has the characteristic rubbery properties of a cured silicone polymer.

U.S. Pat. No. 2,673,823 teaches impregnating a polymer into the interstices of a fabric and thus fully filling the interstices. This patent provides no control of the saturation of the fabric. It teaches full saturation of the interstices of the fabric.

The prior art application of liquid or paste compositions to textiles for purposes of saturation and/or impregnation is typically accomplished by an immersion process. Particularly for flexible webs, including fabric, an immersion application of a liquid or paste composition to the web is achieved, for example, by the so-called padding process wherein a fabric material is passed first through a bath and subsequently through squeeze rollers in the process sometimes called single-dip, single-nip padding. Alternatively, for example, the fabric can be passed between squeeze rollers, the bottom one of which carries the liquid or paste composition in a process sometimes called double-dip or double-nip padding.

Prior art treatment of webs that force a composition into the spaces of the web while maintaining some breathability have relied on using low viscosity compositions or solvents to aid in the flow of the composition. U.S. Pat. No. 3,594,213 describes a process for impregnating or coating fabrics with liquified compositions to create a breathable fabric. This patent imparts no energy into the composition to liquify it while forcing it into the spaces of the web. The composition is substantially liquified before placement onto and into the web. U.S. Pat. No. 4,588,614 teaches a method for incorporating an active agent into a porous substrate. This patent utilizes a solvent to aid in the incorporation of the active agent into the web. The active agent is a non-curable agent since the addition of heat aids in the reduction of viscosity.

One prior art silicone resin composition is taught by U.S. Pat. Nos. 4,472,470 and 4,500,584, and includes a vinyl terminated polysiloxane, typically one having a viscosity of up to about 2,000,000 centipoises at 25° C., and a resinous organosiloxane polymer. The composition further includes a platinum catalyst, and an organohydrogenpolysiloxane crosslinking agent, and is typically liquid. Such composition is curable at temperatures ranging from room temperature to 100° C. or higher depending upon such variables as the amount of platinum catalyst present in the composition, and the time and the temperature allowed for curing.

Such compositions may additionally include fillers, including finely divided inorganic fillers. Silicone resin compositions that are free of any fillers are generally transparent or translucent, whereas silicone resin compositions containing fillers are translucent or opaque depending upon the particular filler employed. Cured silicone resin compositions are variously more resinous, or hard, dependent upon such variables as the ratio of resinous copolymer to vinyl terminated polysiloxane, the viscosity of the polysiloxane, and the like.

Curing (including polymerization and controlled crosslinking) can encompass the same reactions. However, in the fabric finishing arts, such terms can be used to identify different phenomena. Thus, controllable and controlled curing, which is taught by the prior art, may not be the same as control of crosslinking. In the fabric finishing arts, curing is a process by which resins or plastics are set in or on textile materials, usually by heating. Controlled crosslinking may be considered to be a separate chemical reaction from curing in the fabric finishing arts. Controlled crosslinking can occur between substances that are already cured. Controlled crosslinking can stabilize fibers, such as cellulosic fibers through chemical reaction with certain compounds applied thereto. Controlled crosslinking can improve mechanical factors such as wrinkle performance and can significantly improve and control the hand and drape of the web. Polymerization can refer to polymer formation or polymer growth.

Prior art fabrics that exhibit functional properties such as antimicrobial activity, blood repellency, electrical conductivity, fire resistance, and the like, rely on surface coatings or layers of materials to achieve the desired result. Prior art references describe articles having improved performance and functional properties at the expense of comfort and breathability. Greater comfort sacrifices maximum functionality and greater functionality sacrifices comfort.

U.S. Pat. Nos. 4,872,220; 5,024,594; 5,180,585; 5,335,372; and 5,391,423; describe articles that use layers of fabrics and/or polymers to protect against blood, microbes, and viruses from penetrating through the fabrics. U.S. Pat. No. 4,991,232 describes a medical garment comprising a plurality of plies to prevent blood from penetrating through the garment.

Other prior art articles create "zones" upon a thin film surface to impart specific functional properties. For example, U.S. Pat. No. 5,110,683 comprises a semimetallic zone and an electrically insulating zone superimposed on one another. U.S. Pat. No. 5,085,939 describes a thin film-coated polymer web comprising a thin film electronic device on the surface of the thin film. U.S. Pat. No. 4,961,985 describes a coating with specific functional properties attached to the coating.

Accordingly, what is needed in the art are porous articles having improved performance and functional properties, as well as methods for the preparation thereof, while maintaining breathability and hand.

SUMMARY OF THE INVENTION

The present invention includes methods for the treatment of porous webs to controllably cause additives and/or modifiers to orient on and within: (a) a thin film of a polymer composition encapsulating the structural elements (i.e., the fibers or filaments) making up the web, leaving at least some of the interstitial spaces open; (b) an internal layer of a polymer composition between the upper and lower surfaces of the web; or (c) some combination of the foregoing.

The methods of the present invention provide for the controlled placement of modifiers through the manipulation of chemical and physical properties inherent to the modifiers, and the energy controlled viscosity and rheology modified placement of the polymer composition. This is accomplished by 1) optionally pre-treating a web with one or more modifiers through saturation methods known in the art, 2) optionally mixing one or more modifiers with a polymer composition, 3) applying the optionally mixed polymer composition onto a surface of the web, 4) shear thinning the composition and placing it into the web, 5) optionally applying one or more modifiers to the surface of the treated web and forcing the modifier(s) into the web and polymer composition, and 6) curing the polymer composition.

Additives and/or modifiers can be mixed into the polymer composition before, during, and after application of the

composition to a porous web. To apply one or more additives after the polymer composition is applied, the additives are sprayed on prior to curing. The application of pressure causes impregnation of the additives into the top or bottom surfaces of the web and into the polymer composition within the web.

The polymer composition which optionally contains one or more additives or modifiers is applied to the surface of the web. After the polymer is applied to the surface of the web, the polymer composition is preferably immediately shear thinned to controllably and significantly reduce its viscosity and place it into selected places within the web. To aid in this process, the web is preferably distorted, typically by stretching at the location of the shear thinning. This distortion facilitates the entrance of the polymer composition into the web by creating a double or dual shear thinning.

The main energy sources used for orienting the additives are chemical, mechanical, and radiation sources. Chemical sources for orienting additives include, but are not limited to, intermolecular forces such as ionic forces, van der Waals forces, hydrogen bonding forces, polar attraction forces, electrostatic forces, and the like. Mechanical sources refers to the shear thinning that occurs at one or more blades and the pressured application of modifiers at the exit nip rolls. When the polymers reach extremely low viscosities through passing under one or more blades, the shear energy causes the additives or modifiers, comprising either particles or dissimilar molecular weight material, to separate and migrate to the surface of the polymer. Radiation sources include methods for curing the polymer composition. Preferably an oven is used for curing the polymer composition.

Controlled placement of the polymer composition and one or more modifiers within a web may be performed by a basic embodiment of a machine in accordance with the present invention, that is as simple as an applicator to apply viscous polymer to the surface of the web, a pair of facilities for applying tension to a section of the web and a blade forced against the web in the section under tension. The web is pulled under tension past the blade, or, alternatively, the blade is moved relative to the web, and the forces generated by the blade cause the polymer composition to flow into the three-dimensional matrix of the web, and controllably be extracted out of the web leaving one or more modifiers oriented on and within a thin film of polymer encapsulating selected fibers, or an internal layer of polymer, or both. Tension on the web is preferably released thereafter, and the web is cured.

The present invent ion includes novel methods for manufacturing webs, fibers and fabrics that have certain desirable physical and functional qualities by combining the use of encapsulated fibers and filaments and a breathable or controlled pore size internal coating with one or more modifiers described by this invention and a controlled surface chemistry modification. Such webs, fibers and fabrics can be used to prepare a wide variety of products including, but not limited to, carpets, specialized clothing, career apparel, bioengineered surfaces for diagnostic applications, incontinence products, medical garments and upholstery. By use o f the present invention, webs, fibers and fabrics can be manufactured with a wide variety of desired physical and functional characteristics.

Surface chemistry is controlled by using sufficient web tension and front al blade energy to dislodge the fluorochemical or other modifiers from the web which is then caused to surface orient and/or bloom. The webs or fabrics can comprise fibers in the form of monofilaments, yarns, staples, or the like. The webs or fabrics c an also be comprised of a matrix having open cells or pores therein. The webs or fabrics may be a fabric which is woven or non-woven with fibers that can be of any desired composition. The webs or fabrics will generally be tensionable, but not too weak or elastomeric to be processed in accordance with the teachings of the present invention.

Webs treated by the methods of the present invention contain one or more modifiers and a curable or semi-curable polymer or copolymer that may contain monomers that are present as a film, coating, or layer within a web that envelopes or encapsulates at least a portion of the fibers or cell or pore walls of the web. The internal layer is a region generally spaced from the outer surfaces of the web which is substantially continuously filled by the combination of the polymers controllably placed therein and the fibers and filaments of the web in this region. The interstices or open cells in the region of the internal layer are also substantially filled. The outer surfaces of the web are substantially free of any polymer deposits other than the thin film encapsulation of the surface fibers and filaments. However, the web remains breathable, water resistant or waterproof, and exhibits the functionality of the modifier incorporated into the web and/or polymer composition. For example, a web incorporating a synthetic silk-like-protein as the modifier exhibits the functionality of a "silky feel." The thickness of the internal layer is generally in the range of 0.01 to 50 microns.

At a microscopic level, a web treated in accordance with the present invention, for example, a fabric, can be regarded as being a complex structure, but generally the internal layer is discernable under microscopic examination as shown in the accompanying scanning electron microscope photographs that will be discussed hereinafter.

Depending upon the conditions used to produce it, a web produced in accordance with the present invention can characteristically and preferably exhibit a soft hand and flexibility that is comparable to the hand and flexibility of the untreated web. In some cases, the difference between the hand and the feel of the treated and untreated webs may not be perceptible, but may be engineered to be altered through the controlled crosslinking of the polymer. This is particularly surprising in view of the substantial amount of polymer being added to the web. A treated web has a breathability which, by a present preference, can approach a high percentage of the untreated web notwithstanding the relatively large amount of polymer present.

A polymer composition having a starting viscosity in the range of greater than 1,000 centipoise but less than 2,000,000 centipoise is preferably used to produce the treated webs. If desired, additives and/or modifiers can be admixed with such a composition to adjust and improve properties of such composition or web, such as viscosity and/or rheology, combustibility, reflectivity, flexibility, conductivity, light fastness, mildew resistance, rot resistance, stain resistance, grease resistance, and the like. In general, a web treated in accordance with this invention exhibits enhanced durability. These additives are generally controlled by the engineered shear thinning polymer composition and the method and apparatus of this invention to be oriented and surface exposed on the surface of the thin film on the encapsulated fibers, or on one or both surfaces of the internal layer, or on one or both surfaces of the web, or some combination of the above.

A web made by the method of the present invention can preserve much, or even substantially all, of its original

untreated hand, even after an extended period of use, while demonstrating excellent abrasion resistance. In contrast, an untreated web typically loses its original hand and displays reduced abrasion resistance after an extended period of use. This is achieved by the formation of an internal layer that prevents new fiber surfaces from being exposed, thereby minimizing the amount of untreated surfaces, which degrade much faster than the treated fibers.

A web treated by the method of the invention can undergo a large number of machine washings with detergent without experiencing appreciable or significant change or deterioration. The polymer matrix composition prolongs the use and service life of a web, usually by at least an order of magnitude, depending on such factors as web type, extent and type of treatment by the teachings of this invention, and the like.

Optionally, and as indicated above, agents or additives carried by the polymer composition into a web can be stably fixed and selectively placed in the web with the cured polymer. For example, agents such as ultraviolet light absorbers, dulling agents, reflectivity enhancers, antimicrobial agents, proteins, antibodies, pharmaceutical drugs, cell growth promotion materials, flame resistant agents, heat absorbent, anti-static agents, micro spheres containing chemical agents that are time released, and the like, are desirably located substantially upon the surfaces of the web's fibers. When these agents are incorporated into the enveloping polymer film, it appears that they are retained where they are deposited. A present preference for ultraviolet resistant webs in the practice of this invention is to employ a silicone polymer composition that contains a benzophenone.

Various other and further features, embodiments, and the like which are associated with the present invention will become apparent and better understood to those skilled in the art from the present description considered in conjunction with the accompanying drawings wherein presently preferred embodiments of the invention are illustrated by way of example. It is to be expressly understood, however, that the drawings and the associated accompanying portions of this specification are provided for purposes of illustration and description only, and are not intended as limitations on the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph plotting the rheological behavior of polymers used in the practice of this invention.

FIG. 2 is a schematic vector diagram illustrating surface tension forces.

FIG. 3 is a graph relating contact angle over a smooth, solid surface.

FIG. 4 illustrates diagrammatically one embodiment of a blade suitable for use in an apparatus used in the practice of the present invention.

FIG. 5 illustrates diagrammatically a presently preferred embodiment of an apparatus suitable for use in the practice of the present invention.

FIGS. 6a through 6g are scanning electron microscopy (SEM) photomicrographs and elemental analyses which depict various results in fabrics, fibers and filaments from back scatter evaluation tests.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following description includes the best presently contemplated mode of carrying out the invention. This

description is made for the purpose of illustrating the general principles of the inventions and should not be taken in a limiting sense.

In accordance with the present invention there are provided porous articles comprising a porous web having a curable, thixotropic material and one or more modifiers therein.

In a particular aspect of the present invention, the curable, thixotropic material and modifiers form an internal, continuous layer located between the upper and lower surfaces of the porous web. In another aspect of the present invention, the curable, thixotropic material and modifiers substantially encapsulate the fibers of the fabric web. In still another aspect of the invention, the modifier is selectively positioned within the web.

In a particular specific aspect of the invention, the modifier is selectively positioned substantially on or within the encapsulating material, or substantially on or within the internal continuous layer, or substantially on or within one or more surfaces of the web.

In accordance with another embodiment of the invention, there is provided a method of controllably applying a combination of treating materials to a porous web, said method comprising: applying a curable, thixotropic material and one or more modifiers to a porous web; and subjecting said thixotropic material and modifier(s) to sufficient energy to cause the thixotropic material and modifier(s) to flow into the porous web without substantially blocking the interstitial spaces thereof.

In a preferred aspect of this embodiment, sufficient energy is applied to selectively position the modifier substantially on or within the enveloping material or substantially on or within the internal, continuous layer, or some combination of the foregoing.

In yet another embodiment of the present invention, there are provided novel compositions containing one or more compounds that impart specific functional properties into articles manufactured from the treated webs.

The present invention relates to methods and apparatus for manufacturing a treated web with one or more modifiers incorporated therein. The subject methods and apparatus involve the control of numerous process variables, including, without limitation, web tension (both overall web tension as well as the web tension immediately before and after each individual blade), angle of entry of web in contact with each blade, blade angle in relation to horizontal reference point, blade pressure against moving web, angle of exit of web from contact with each blade, web speed, number of blades, the pressure of the exit nip rolls, thickness of each blade, oven cure temperature, oven cure dwell time, blade surfaces and edge conditions, blade finish, and the like.

Other variables that affect the finished product, but are not directly related to the methods and apparatus, include, without limitation, the polymer blend, the starting viscosity of the polymer composition, accelerators added to the polymer composition, additives added to the polymer composition, the type of web used, ambient temperature, humidity, airborne contaminants, lint on web, pre-treatment of web, sub-web surface temperature, web moisture content, and the like.

With respect to the blades, the blade frontal and trailing edges and the finish of the surfaces that meet to make these edges, are important. A hard, smooth surface of both blade face and edges is desirable to shear thin the polymer and keep it flowing and to maximize friction or selectively create shear forces between the web, the polymer, and blade(s). For

some applications, the blades should preferably remain rigid in all dimensions and have minimal resonance in order to achieve uniform web treatment.

The apparatus used for orienting one or more modifiers on and within a web has facilities for rotating the angle of each blade ±90° from the vertical. In order to vary the shear and placement forces of the blade against the web, polymer and additives, adjustment facilities are provided for moving the blade vertically up and down and moving the blade forward and backward horizontally. All three axes are important for creating the desired control which causes additives and/or modifiers to orient on and within (a) thin film encapsulation of the individual fibers and filaments (b) the controlled placement of the internal coating, and (c) some combination of (a) and (b). The lateral placement of each blade relative to the other is also important and facilities are provided for allowing lateral movement of each blade toward and away from each other. The lateral placement of each blade controls the micro tension and elastic vibration of the web between the preceding roll and the blade, thereby controlling the web after the immediate exit of the web from the blade and controlling the Coanda Effect, as described in U.S. Pat. No. 4,539,930, so that controlled placement of the internal layer takes place.

Changing the tension of the web results in changes internally in the web, such as the position of the internal layer of the web, as well as how much or how little fiber encapsulation occurs, and the thickness of the film encapsulating the individual fibers or filaments. Tension causes the web to distort. This distortion facilitates the entrance of the polymer composition into the web by creating a double or dual shear thinning. In the case of the web, this is produced by the combination of the edge condition of the blade, the engineered shear thinnable polymer, the speed of the web, and the subsequent repositioning of the fibers and filaments after their immediate passage under the edge of the blade.

At the leading edge of the blade, the web is stretched longitudinally and the polymer is simultaneously and dynamically shear thinned, placed into the web, and partially extracted from the web, thereby leaving encapsulated fibers and filaments and/or an internal layer. As the web passes the leading edge of the blade, the elastic recovery forces of the web combined with the relaxation or elastic recovery of the fibers and filaments causes fiber encapsulation and the surface chemistry modification (or bloom). It is believed that this occurs by the popping apart of the individual fibers and filaments. The fibers and filaments either pull the polymer from the interstitial spaces or the rheology of the polymer attracts it to the fibers and filaments or some combination of the two. The end result is that the polymer in the interstitial spaces moves to the fibers and filaments as they move or snap apart, thereby creating encapsulated fibers and filaments. Additives and/or modifiers optionally mixed into the polymer composition are physically positioned within the web and within the polymer at the leading edge of the blade. At the bottom surface of the blade, the thickness, depth, and controlled placement of the internal layer is determined. A wider blade results in a thicker internal layer of polymer. Further, the dynamics of stretch and relaxation of the fibers provides for an even distribution of energy necessary for the thin film encapsulation of the polymer composition over the fibers.

Passing the treated web through the exit nip rolls pushes the fibers or structural elements of the web together. Just prior to passing the treated web through the exit nip rolls, one or more modifiers can be topically applied to the web, thereby forcing the modifier(s) onto and into one or more surfaces of the web. The modifier can adhere to the web and/or the polymer composition in the web. Preferably the modifier(s) adheres to the polymer composition (which encapsulates the individual fibers or filaments, that forms an internal layer, that fills the interstitial spaces of the web, or that produces some combination of the foregoing). The hardness of and the material of the exit nip rolls affects the finished web. The exit nip rolls could be either two rubber rolls or two steel rolls, or one steel roll and one rubber roll, and the rubber rolls could be of different durometers. Further, the variation of the hardness of one or both nip rolls changes the contact area or footprint between the nip rolls and the web as the web passes therebetween. With a softer roll there is a larger contact area and the web is capable of retaining the controlled placement of additives and/or modifiers to orient on and within the: (a) thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) some combination of (a) and (b). With a harder roll there is a smaller contact area which is appropriate for heavier webs.

Additional controllable variables include the various controls of each blade, the nip rolls durometer, the nip release effect, the nip surface characteristics, the guidance, and the pre-treatment of the substrate. Some of the controllable variables are: 1) web tension, 2) angle of entry of fabric into the blade, 3) blade angle in reference to horizontal position, 4) blade pressure against fabric (blade height), 5) angle of exit of fabric from blade, 6) web speed, 7) number of blades, 8) initial rheology and viscosity of polymers, 9) nip pressure, 10) entry nip pressure, 11) additional nip stands that divide the tension zone into multiple tension areas with blades in one or more of the tension areas, 12) blade thickness and shape, 13) polymers and polymer blends, 14) accelerators and inhibitors added to polymers, 15) additives and/or modifiers in polymers, 16) oven cure temperature, 17) oven cure dwell time, 18) substrate type, 19) ambient polymer temperature, 20) humidity, and the like. Controlling the above variables affects orientation of additives and/or modifiers on and within the (a) thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) some combination of (a) and (b).

An increase in web tension causes less polymer to be applied to the web, and also, more of what is applied to be extracted from the web. Web tension occurs between the entrance pull stand and the exit pull stand (see FIG. 5). The primary tension is a result of the differential rate between the driven entrance pull stand and the driven exit pull stand whereby the exit pull stand is driven at a rate faster than the entrance pull stand. Other factors which effect tension are (1) the blade roll diameter, (2) the vertical depth of the blade(s), (3) the durometer of the entrance pull stand roll and rubber roll of the exit pull stand, and (4) the friction as the web passes under the blade(s). The larger the blade roll diameter, the higher the tension of the web. If the drive rate of the web remains constant, then increasing the depth of the blade into the web creates a greater micro tension condition under the blade. Similarly, decreasing the depth into the web decreases the micro tension under the blade. The lower the durometer of the entrance pull stand roll and rubber roll of the exit pull stand, the larger the footprint or contact area between the rolls. A larger footprint produces more surface friction, thereby limiting web slippage and increasing the potential for web tension. Likewise, web slippage can be effected by changing the surface texture of the rolls, i.e., a smooth roll will allow greater slippage than a highly contrasting or rough surface texture. Increasing friction, as the

fabric passes under the blade(s), also produces tension. Friction is a function of the surface area of the bottom of the blade(s). Increasing the surface area increases the friction which increases the tension.

The angle of entry of web in contact with the blade(s) can be varied by blade roll height, blade roll diameter, blade angle, distance between prior blade roll(s) and blade(s), and height of the blades. Increasing the blade roll height and blade roll diameter increases the angle of exit of web from contact with the blade. Rotating the blade angle clockwise from the perpendicular, with the web running left to right, increases the angle of entry of web in contact with the blade(s). Likewise, rotating the blade angle counter-clockwise from the perpendicular, with the web running left to right, decreases the entry angle. Decreasing the distance between the roll before the blade and the blade decreases the contact angle. Increasing the downward depth of the blade(s) into the web decreases the contact angle with the blade(s).

The angle of the blade(s) is completely changeable and fully rotational to 360°. The fully rotational axis provides an opportunity for more than one blade per rotational axis. Therefore, a second blade having a different thickness, bevel, shape, resonance, texture, or material can be mounted. Ideally, apparatus employed in the practice of the present invention contains two or three blades per blade mount.

The blade height or blade pressure applied against a web can be obtained through the vertical positioning of the blade(s) in the blade mount. The greater the downward depth of the blade(s), the greater the pressure. Blade pressure against the web is also accomplished through the tension applied to the web, as described above.

The same line components that affect the angle of entry of web in contact with the blade(s), also affect the angle of exit of web from contact with the blade(s). Any changes in blade roll(s) vertical height, diameter, or distance away from the blade, affects the exit angle of the web. If the angle of the blade is rotated clockwise as described above, the entry angle of the web increases, thus decreasing the exit angle.

Web speed is proportional to the variable speed of the motor which drives the entrance and exit nip stands. Web speed can effect the physics of the polymers as the web passes under the blades.

The number of blades can vary. Generally, more than one blade is required. The polymer is first applied onto the web prior to the first blade but can also be applied prior to additional blade positions. At each blade, a rolling bead of polymer can exist at the interface of the blade and the web (entry angle). Basically, a high viscosity polymer is applied and through the process of shear thinning, the viscosity is greatly decreased, allowing the polymer to enter into the interstitial spaces of the web. Any blade(s) after the first blade, serves to further control the polymer rheology and viscosity and continue the controlled placement of the polymer into the web. This is accomplished by controllably removing excess polymer to obtain an even distribution of polymer to any area, or a combination of the three areas of a) the thin film encapsulation of the individual fibers and filaments, b) the controlled placement of the internal layer, and c) the controlled placement of the additives in a) and b).

The initial process dynamics for the rheology and viscosity of the polymer are designed and engineered with the required attributes to achieve orientation of additives and/or modifiers on and within the (a) thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal layer, and (c) some combination of (a) and (b). If the polymer viscosity is high, the polymer may need to be pre-thinned.

The entrance pull stand is a driven roll proportionally driven at a predetermined rate slower than the exit pull stand (see FIG. 5). The entrance and exit pull stands are adjustable from about 100 pounds of force to 5 or more tons of force. The bottom rolls of both the entrance and exit pull stands have micro-positioning capability to provide for gap adjustment and alignment. The composition of the top roll of the entrance and exit pull stands is chosen based on the durometer of the urethane or rubber. The top roll of the exit pull stand preferably utilizes a Teflon sleeve which will not react with the polymers used in the process. The bottom roll of the exit pull stand is preferably chrome plated or highly polished steel to reduce the impression into the preplaced polymer in the web.

An additional nip stand can be added between the blades to divide the tension zone into multiple tension areas with blades in one or more of the tension areas. This enables the operator to adjust the tension at any one blade and to therefore control the placement of the additives into and onto the web by controlling the placement of the polymer composition.

Blade thickness and shape have substantial effects on the movement of the structural elements of the web during processing and more importantly, the viscoelastic flow characteristics of the polymer in controlling the orientation of the additives and/or modifiers on and within the (a) thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal layer, and (c) some combination of (a) and (b). The blade bevel can effect the entry angle of the web and effect the sharpness of the leading edge of the blade. A sharper leading edge has a greater ability to push the weave or structural elements of the web longitudinally and transversely, increasing the size of the interstitial spaces. As the web passes the leading edge of the blade, the interstitial spaces snap back or contract to their original size. The polymer viscosity is reduced and the polymer is placed into the web at the leading edge of the blade. Blade thickness and shape effects the polymers and their selected additives and the placement thereof. Preferably, the combination of the leading edge condition and the two surfaces (the front and the bottom) that meet at the leading edge are RMS 8 or better in grind and/or polish. This creates a precise leading edge; the more precise the leading edge, the more the shear thinning control.

There are a number of pre-qualifiers or engineered attributes of polymers that enhance control of flow and orientation of additives and/or modifiers on and within the (a) thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) some combination of (a) and (b). Blending polymers is one way to achieve ideal flow and placement characteristics. An example of a blended polymer is where one polymer, selected for its physical properties, is mixed with another polymer that is selected for its viscosity altering properties. Many tests using different polymer blends have been done. Polymer blends vary by both chemical and physical adhesion, durability, cure dwell time required, cure temperature required, flexibility, percentage add-on required, performance requirements, and aesthetics.

Accelerators and inhibitors which are added to polymers, generally produce three effects. An illustrative accelerator or inhibitor is a platinum catalyst, which is a cure or crosslinking enhancer. The first effect it produces is to control the time and temperature of the web as it cures. A cure or controlled crosslinking enhancer can significantly assist in controlling the drape and hand feel of the web. The second effect is to alter the cure to allow the web to reach partial

cure and continue curing after leaving an initial heat zone. This second effect also assists in retaining the drape and hand feel of the web. The third effect of inhibitors is to achieve a semi-cure for later staging of the cure.

Additives which are added to the polymers significantly control surface chemistry. Surface chemistry characteristics are controlled by including additives that have both reactive and bio-interactive capabilities. The method and apparatus of this invention can control the placement of the additives on the surface of the thin film encapsulating the fibers, on either or both surfaces of the internal layer, on either or both surfaces of the web, or any combination of the foregoing.

The oven cure temperature and the source and type of cure energy, are controlled for a number of reasons. The oven cure temperature is controlled to achieve the desired crosslinked state; either partial or full. The source and type of energy can also affect the placement of the polymer and additives. For example, by using a high degree of specific infrared and some convection heat energy for cure, some additives can be staged to migrate and/or bloom to the polymer surfaces.

Oven cure temperature is thermostatically controlled to a predetermined temperature for the web and polymers used. Machine runs of new webs are first tested with hand pulls to determine adhesion, cure temperature, potentials of performance values, drapability, aesthetics, etc. The effect on the web depends on the oven temperature, dwell time and curing rate of the polymer. Webs may expand slightly from the heat.

Oven cure dwell time is the duration of the web in the oven. Oven cure dwell time is determined by the speed of the oven's conveyor and physical length of the oven. If the dwell time and temperature for a particular web is at maximum, then the oven conveyor speed would dictate the speed of the entire process line or the length of the oven would have to be extended in order to increase the dwell time to assure proper final curing of the web.

The physical construction and chemistry of the web is critical. The amount of control over the rheology of the polymer and the tension on the web are dependent on the physical construction and chemistry of the web and chemistry of the composition(s) applied to the web. The web selected for use in the practice of the present invention must have physical characteristics that are compatible with the flow characteristics of the polymer to achieve the desired results.

The ambient polymer temperature refers to the starting or first staging point to controlling the viscosity and rheology. The process head can control the ambient polymer temperature through temperature controlled polymer delivery and controlled blade temperatures.

Humidity can sometimes inhibit or accelerate curing of the polymer. Therefore, humidity should be monitored and, in some conditions, controlled.

In view of the fact that between the shear thinning stations and the oven, the polymer composition may begin to set or partially cure, it may be desirable to overshear so that by the time the web reaches the curing oven, it will be at the point where it is desired that the cure occur. This over shear effect is a matter of controlling certain variables, including the force of the blades against the moving web, as well as the tension and speed of the web.

By having a number of shear thinning blades, a multiple shear thinning effect is created, which changes the final construct of the polymer and the (a) thin film encapsulation of the individual fibers and filaments, (b) controlled placement of the internal coating, and (c) controlled placement of

the additives in (a) and (b). It is understood that the first shear thinning causes viscoelastic deformation of the polymer composition which, due to its memory, tends to return to a certain level. With each multiple shear thinning, the level to which the polymer starts at that shear point and returns is changed (see FIG. 1). This is called thixotropic looping or plateauing.

Definitions

As employed herein, the term "adhesiveness" refers to the capacity to bind other solids by both chemical and physical means.

The phrase "antistatic character," as used herein refers to the capacity to reduce the generation of charge, increase the rate of charge dissipation, inhibit the production of charge, or some combination of the foregoing.

The phrase "biocidal activity," as used herein, refers to the capacity of a compound to kill pathogenic and/or non-pathogenic microorganisms, and prevent or inhibit the action or growth of microorganisms including viruses and bacteria. Biocidal activity can be measured by applying Test Methods 100-1993, 147-1993, and 174-1993 of the Technical Manual of the American Association of Textile Chemist and Colorist (AATCC), Dow Corning Corporate Test Method 0923, and the Kirby-Bauer Standard Antimicrobial Susceptibility Test as described in the Manual of Clinical Microbiology, Fourth Edition, all of which are incorporated herein by reference.

As employed herein, the term "biocide" refers to any physical or chemical agent capable of combating pathogenic and non-pathogenic microorganisms, including bacteria and viruses.

As employed herein, the phrase "biological activity" refers to the functionality, reactivity, and specificity of compounds that are derived from biological systems or those compounds that are reactive to them, or other compounds that mimic the functionality, reactivity, and specificity of these compounds. Examples of suitable biologically active compounds include enzymes, antibodies, antigens and proteins.

The term "breathability," as used herein, refers to gas permeability such as the moisture vapor transmission of a material as measured by ASTM E96 and the specifically developed modified "Bellow's Test" described in subsequent sections.

The term "coating" as used herein, refers to a generally continuous film or layer formed by a material over or on a surface.

As employed herein, the phrase "color fastness" refers to the capacity of a fabric to resist fading during a period of normal wear and multiple washings and dry cleaning. Color fastness is determined under conditions of accelerated weathering.

With respect to the polymer compositions used in this invention, the term "controlled placement" or "placement" refers to the penetration of such polymer compositions into a porous web, to the distribution of such composition in a controlled manner through such web, and to the resultant, at least partial envelopment of at least a portion of the fibers of such web by such composition in accordance with the present invention, or to the formation of an internal layer, or both.

The term "curing", or "cure", as used herein, refers to a change in state, condition, and/or structure in a material, such as a curable polymer composition that is usually, but not necessarily, induced by at least one applied variable, such as time, temperature, radiation, presence and quantity in such material of a curing catalyst or curing accelerator, or

the like. The term "curing" or "cured" covers partial as well as complete curing. In the occurrence of curing in any case, such as the curing of such a polymer composition that has been selectively placed into a porous flexible substrate or web, the components of such a composition may experience occurrence of one or more of complete or partial (a) polymerization, (b) cross-linking, or (c) other reaction, depending upon the nature of the composition being cured, application variables, and presumably other factors. It is to be understood that the present invention includes polymers that are not cured after application or are only partially cured after application.

As employed herein, the term "durability" refers to the capacity of a fabric to retain its physical integrity and appearance during a period of normal wear and multiple washings and dry cleaning.

The term "elastomeric" as used herein refers to the ability of a cured polymer treated web to stretch and return to its original state.

The phrase "electrical conductivity," as used herein refers to the capacity to conduct electrical current.

The phrase "electromagnetic radiation absorptivity," as used herein, refers to the absorption of radiation of wavelengths from within the electromagnetic spectrum.

The phrase "electromagnetic shielding capacity," as used herein, refers to the capacity to reflect, absorb, or block electromagnetic radiation.

The term "envelop" or "encapsulate" as used interchangeably herein, refers to the partial or complete surrounding, encasement, or enclosing by a discrete layer, film, coating, or the like, of exposed surface portions of at least some individual fiber or lining of a cell or pore wall of a porous web. Such a layer can sometimes be contiguous or integral with other portions of the same enveloping material which becomes deposited on internal areas of a web which are adjacent to such enveloping layer, enveloped fiber, lined cell or pore wall, or the like. The thickness of the enveloping layer is generally in the range of 0.01 to 50 microns, and preferably in the range of about 0.1 to 20 microns.

The term "fiber", as used herein, refers to a long, pliable, cohesive, natural or man-made (synthetic) threadlike object, such as a monofilament, staple, filament, or the like. A fiber usable in this invention preferably has a length at least 100 times its diameter or width. Fibers can be regarded as being in the form of units which can be formed by known techniques into yarns or the like. Fibers can be formed by known techniques into woven or non-woven webs (especially fabrics) including weaving, knitting, braiding, felting, twisting, matting, needling, pressing, and the like. Preferably, fibers, such as those used for spinning, as into a yarn, or the like, have a length of at least about 5 millimeters. Fibers such as those derived from cellulosics of the type produced in paper manufacture can be used in combination with longer fibers as above indicated, as those skilled in the art will readily appreciate.

The term "filament" as used herein refers to a fiber of indefinite length.

The term "filled" as used herein in relation to interstices, or interstitial spaces, or open cells, and to the amount of polymer composition therein in a given web, substrate, or the fibers in such web or substrate, designates the presence of such composition therein. When a given interstitial space or open cell is totally taken up by such composition, it is "completely filled" or "plugged". The term "filled" also refers to an interstitial space having a film or layer of polymer composition over or through it so that it is closed even though the entire thickness of the interstitial space is not completely filled or plugged.

Measurements of the degree of envelopment, interstitial fillage, plugging, or the like in an internal coating are conveniently made by microscopy, or preferably by conventional scanning electron microscopy (SEM) techniques. Because of the nature of such measuring by SEM for purposes of the present invention, "a completely filled" interstitial space or open cell can be regarded as a "plugged" interstitial space or open cell.

The term "flattening agent," as used herein, refers to a compound that dulls the finish on glossy fabrics.

The term "flow" or "flowability" as used herein means the altering of the rheology of a material by the application of energy to a suitable material so as to allow the flowing of the material to form: (a) a thin film of a polymer composition encapsulating the structural elements (i.e., the fibers or filaments) making up the web leaving at least some of the interstitial spaces open; (b) an internal layer of a polymer composition between the upper and lower surfaces of the web; or (c) some combination of the foregoing.

The phrase "fluid resistance," as used herein, refers to the ability of a material to resist the penetration of fluids. Fluid resistance is measured by the Rain test, Suter test, and hydrostatic resistance measurements, discussed in the "Examples" section and incorporated herein by reference. Fluid resistance, for purposes of the present invention, is the result of two conditions. First, the surface of the web has the potential for increased fluid resistance due to the choice of the polymer and also the choice of additives and/or modifiers to control surface energies. Second, the external fluid resistant or fluid proof properties can be altered by controlling the effective pore size of the web. Additives and/or modifiers can serve to increase or decrease the effective pore size by controlling the viscosity and rheology achieved through the processing of polymer in the machine. In addition, the bimodal distributions of pore sizes found in a woven fabric are controlled by the processing. The larger pore sizes are supplied by the spaces between yarns while smaller pores reflect the yarn structure and the polymer composition pore size.

As employed herein, the term "functional" refers to a particular performance attribute such as biocidal activity, therapeutic activity, ion-exchange capacity, biological activity, biological interactive capacity to bind compounds, surface chemistry activity, electromagnetic radiation absorptivity, adhesiveness, hand, durability, color fastedness, light reflectivity, fluid resistance, waterproofness, breathability, mildew resistivity, rot resistivity, stain resistivity, electrical conductivity, thermal conductivity, antistatic character, processability, rheological character, electromagnetic shielding capacity, and radio frequency shielding capacity.

The term "hand" refers to the tactile feel and drapability or quality of a fabric as perceived by the human hand.

With respect to the fluorochemical liquid dispersions (or solutions) which can optionally be used for web pretreatment, the term "impregnation" refers to the penetration of such dispersions into a porous web, and to the distribution of such dispersions in a preferably, substantially uniform and controlled manner in such web, particularly as regards the surface portions of the individual web component structural elements and fibers.

The term "internal coating or internal layer" as used herein, refers to a region generally spaced from the outer surfaces of the web which is substantially continuously filled by the combination of the polymer controllably placed therein and the fibers and filaments of the web in the specified region. Such coating or layer envelopes, and/or

surrounds, and/or encapsulates individual fibers, or lines cell or pore walls of the porous web or substrate, in the specified region. The internal layer is not necessarily flat but may undulate or meander through the web, occasionally even touching one or both surfaces of the web. Generally, the internal layer is exposed on both sides of a web as part of the multi complex structure of a woven and non-woven web. The thickness of the internal layer is generally in the range of 0.01 to 50 microns, and preferably in the range of about 0.1 to 20 microns.

As used herein, the phrase "ion-exchange capacity" refers to the capacity to exchange mobile hydrated ions of a solid, equivalent for equivalent, for ions of like charge in solution.

The phrase "light reflectivity," as used herein, refers to the capacity to reflect light from the visual region of the electromagnetic spectrum.

The phrase "mildew resistance," as used herein, refers to the capacity to either kill or prevent or inhibit the growth of mildew. Mildew resistance can be quantified by Test Method 30-1993 of the Technical Manual of the American Association of Textile Chemist and Colorist (AATCC), incorporated herein by reference.

The term "modifiers," "agents," or "additives," used interchangeably herein, refers to materials and compounds that impart or alter specific physical or chemical characteristics with respect to the articles produced therefrom. These physical or chemical characteristics are typically functional properties. The modifiers may also alter or impart functional properties to the thixotropic material. Examples of modifiers suitable for use in the practice of the present invention include biocides, therapeutic agents, nutrients, adhesive agents, humidity-controlling agents, water repellents, ion-exchange agents, light-reflective agents, dyes and pigments, mildew-resistance agents, conductive agents, proteins, hand-altering agents, blood repellents, flexibility-inducing agents, light fastness-inducing agents, rot-resistant agents, stain-resistant agents, grease-resistant agents, ultraviolet-absorbing agents, fillers, flattening agents, electrical conductive agents, thermal conductive agents, flame retardants, antistatic agents, electromagnetic shielding agents, and radio frequency shielding agents. Examples of suitable nutrients which can be employed in the practice of the present invention include cell growth nutrients.

The term "polymer", or "polymeric" as used herein, refers to monomers and oligomers as well as polymers and polymeric compositions, and mixtures thereof, to the extent that such compositions and mixtures are curable and shear thinnable.

As employed herein, the term "processability" refers to the nature of a material with respect to its response to various processing methods and process parameters. Processing agents contemplated for use in the practice of the present invention could also include cross-link inhibitors that either delay the onset of cure or slow the cure rate of the curable, thixotropic material, and thixotropy inducing or rheological agents that, for example, alter the viscosity of the curable material, and the like.

The phrase "radio frequency shielding capacity," as used herein, refers to the capacity to reflect, absorb, or block radio frequency waves.

As employed herein, the phrase "rheological character" refers to material attributes such as flow, viscosity, elasticity, and the like.

As employed herein, the phrase "rot resistance" refers to the capacity to prevent or inhibit the decay of naturally-derived materials.

The term "shear thinning," in its broadest sense, means the lowering of the viscosity of a material by the application of energy thereto.

The phrase "stain resistance," as used herein, refers to the ability of a material to resist coloring by a solution or a dispersion of colorant. Waterborne stain resistance refers to the ability to resist coloring by a waterborne stain.

As employed herein, the quantity meant by the term "sufficient" will depend on the nature of the energy source, the porous substrate, the curable, thixotropic material, the additives and/or modifiers used, and the desired functional properties of the article produced therefrom. A description of the method and several examples are provided to provide enough guidance to on e of skill in the art to determine the amount of energy require d to practice this invention.

As employed herein, the phrase, "surface chemistry activity" refers to the composition, reactivity, and positioning of chemical moities on the surfaces of the porous substrate. As contemplated for use in the practice of the present invention, modifiers that alter the surface chemistry of the resulting article include fluorochemical compounds, proteins, and any other modifier compound that can be selectively positioned at the various surfaces within the porous substrate.

The phrase "therapeutic activity," as employed herein, refers to the capacity to treat, cure, or prevent a disease or condition. As employed herein, the term "therapeutic agents" refers to compound(s) that are effective at treating, curing, or preventing a disease or condition.

The phrase "thermal conductivity," as us ed herein refers to the capacity to conduct heat.

The word "thixotropy" refers herein to liquid flow behavior in which the viscosity of a liquid is reduced by shear agitation or stirring so as to allow the placement of the liquid flow to form: (a) a thin film of a polymer composition encapsulating the structural elements (i.e., the fibers or filaments) making up the web leaving at least some of the interstitial spaces open; (b) an internal layer of a polymer composition between the upper and lower surfaces of the web; or (c) some combination of the foregoing. It is theorized to be caused by the breakdown of some loosely knit structure in the starting liquid that is built up during a period of rest (storage) and that is broken down during a period of suitable applied stress.

As employed herein, the phrase "waterproofness" refers to the wetting characteristic of a material with respect to water. Waterproofness is measured using the Mullen Test, Federal Standard 191, method 5 512, incorporated herein by reference.

The term "web" as used herein is intended to include fabrics and refers to a sheet-like structure (woven or non-woven) comprised of fibers or structural elements. Included with the fibers can be non-fibrous elements, such as particulate fillers, binders, dyes, sizes and the like in amounts that do not substantially affect the porosity or flexibility of the web. While preferably, at least 50 weight percent of a web treated in accordance with the present invention is fibers, more preferred webs have at least about 85 weight percent of their structure as fiber. It is presently preferred that webs be untreated with any sizing agent, coating, or the like, except as taught herein. The web may comprise a laminated film or fabric and a woven or non-woven porous substrate. The web may also be a composite film or a film laminated to a porous substrate or a double layer.

The term "webs" includes flexible and non-flexible porous webs. Webs usable in the practice of this invention can be classified into two general types:

(A) Fibrous webs; and

(B) Substrates having open cells or pores, such as foams.

A porous, flexible fibrous web is comprised of a plurality of associated or interengaged fibers or structural elements

having interstices or interstitial spaces defined therebetween. Preferred fibrous webs can include woven or non-woven fabrics. Other substrates include, but are not limited to, a matrix having open cells or pores therein such as foams or synthetic leathers.

The term "yarn" as used herein refers to a continuous strand comprised of a multiplicity of fibers, filaments, or the like in a bundled form, such as may be suitable for knitting, weaving or otherwise used to form a fabric. Yarn can be made from a number of fibers that are twisted together (spun yarn) or a number of filaments that are laid together without twist (a zero-twist yarn).

A flexible porous web used as a starting material in the present invention is generally and typically, essentially planar or flat and has generally opposed, parallel facing surfaces. Such a web is a three-dimensional structure comprised of a plurality of fibers with interstices therebetween or a matrix having open cells or pores therein. The matrix can be comprised of polymeric solids including fibrous and non-fibrous elements.

Three principal classes of substrates having open pores or cells may be utilized in the present invention: leathers (including natural leathers, and man-made or synthetic leathers), foamed plastic sheets (or films) having open cells, and filtration membranes.

Foamed plastic sheet or film substrates are produced either by compounding a foaming agent additive with resin or by injecting air or a volatile fluid into the still liquid polymer while it is being processed into a sheet or film. A foamed substrate has an internal structure characterized by a network of gas spaces, or cells, that make such foamed substrate less dense than the solid polymer. The foamed sheets or film substrates used as starting materials in the practice of this invention are flexible, open-celled structures.

Natural leathers suitable for use in this invention are typically split hides. Synthetic leathers have wide variations in composition (or structure) and properties, but they look like leather in the goods in which they are used. For purposes of technological description, synthetic leathers can be divided into two general categories: coated fabrics and poromerics.

Synthetic leathers which are poromerics are manufactured so as to resemble leather closely in breathability and moisture vapor permeability, as well as in workability, machinability, and other properties. The barrier and permeability properties normally are obtained by manufacturing a controlled microporous (open celled) structure. Synthetic leathers which are coated fabrics, like poromerics, have a balance of physical properties and economic considerations. Usually the coating is either vinyl or urethane. Vinyl coatings can be either solid or expanded vinyl which has internal air bubbles which are usually a closed-cell type of foam. Because such structures usually have a non-porous exterior or front surface or face, such structures display poor breathability and moisture vapor transmission. However, since the interior or back surface or face is porous, such materials can be used in the practice of this invention by applying the curable, thixotropic material and one or more modifier to the back face thereof.

Filtration membranes contemplated for use in the practice of the present invention include microporous membranes, ultrafiltration membranes, asymmetric membranes, and the like. Suitable membrane materials include polysulfone, polyamide, polyimide, nitrocellulose, cellulose acetate, nylon and derivatives thereof.

Other porous webs suitable for use in the practice of the present invention include fibers, woven and non-woven fabrics derived from natural or synthetic fibers, papers, and the like. Examples of papers are cellulose-based and glass fiber papers.

The fibers utilized in a porous flexible web treated by the methods and apparatus of the present invention can be of natural or synthetic origin. Mixtures of natural fibers and synthetic fibers can also be used. Examples of natural fibers include cotton, wool, silk, jute, linen, and the like. Examples of synthetic fibers include acetate, polyesters (including polyethyleneterephthalate), polyamides (including nylon), acrylics, olefins, aramids, azlons, glasses, modacrylics, novoloids, nytrils, rayons, sarans, spandex, vinal, vinyon, regenerated cellulose, cellulose acetates, and the like. Blends of natural and synthetic fibers can also be used.

A porous web or fabric is preferably untreated or scoured before being treated in accordance with the present invention. Preferably a web can be preliminarily treated, preferably saturated, for example, by padding, to substantially uniformly impregnate the web with a fluorochemical. Typically, and preferably, the treating composition comprises a dispersion of fluorochemical in a liquid carrier. The liquid carrier is preferably aqueous and can be driven off with heat after application. The treating composition has a low viscosity, typically comparable to the viscosity of water or less. After such a treatment, it is presently preferred that the resulting treated web exhibits a contact angle with water measured on an outer surface of the treated web that is greater than about 90 degrees. The treated web preferably contains fluorochemical substantially uniformly distributed therethrough. Thus, the fluorochemical is believed to be located primarily on and in the individual fibers, cells or pores with the web interstices or open cells being substantially free of fluorochemical.

A presently preferred concentration of fluorochemical in a treatment composition is typically in the range of about 1 to about 10% fluorochemical by weight of the total treating composition weight, and more preferably is about 2.5% of an aqueous treating dispersion. Web weight add-ons of the fluorochemical can vary depending upon such factors as the particular web treated, the polymer composition to be utilized in the next step of the treatment process of this invention, the ultimate intended use and properties of the treated web of this invention, and the like. The fluorochemical weight add-on is typically in the range of about 0.01 to about 5% of the weight of the untreated web.

After fluorochemical controlled placement, the web is preferably squeezed to remove excess fluorochemical composition after which the web is heated or otherwise dried to evaporate carrier liquid and thereby also accomplish fluorochemical insolubilization or sintering, if permitted or possible with the particular composition used.

The fluorochemical treated web thereafter has a predetermined amount of a curable polymer composition controllably placed within the web by the methods and apparatus of this invention, to form a web whose fibers, cells or pores are at least partially enveloped or lined with the curable polymer composition, whose web outer surfaces are substantially free of the curable polymer, whose web interstices or open cells are not completely filled with the curable polymer and which may also contain an internal layer of polymer. The curable polymer composition utilized preferably exhibits a starting viscosity greater than 1,000 centipoise and less than 2,000,000 centipoise at rest at 25° C. at a shear rate of 10 reciprocal seconds.

The fluorochemical residue that remains after web treatment may not be exactly evenly distributed throughout the web, but may be present in the web in certain discontinuities.

For example, these discontinuities may be randomly distributed in small areas upon an individual fiber's surface. However, the quantity and distribution of fluorochemical through a web is believed to be largely controllable. Some portions of the fluorochemical may become dislodged from the web and migrate through the polymer due to the forces incurred by the shear thinning and controlled placement of the polymer.

The curable polymer composition is believed to be typically polymeric, (usually a mixture of co-curable polymers and oligomers), and to include a catalyst to promote the cure. The polymers that can be used in the present invention may be monomers or partially polymerized polymers commonly known as oligomers, or completely polymerized polymers. The polymer may be curable, partially curable or not curable depending upon the desired physical characteristics of the final product. The polymer composition can include conventional additives.

While silicone is a preferred composition, other polymer compositions include polyurethanes, fluorosilicones, silicone-modified polyurethanes, acrylics, polytetrafluoroethylene-containing materials, and the like, either alone or in combination with silicones.

It is to be understood that the depth of polymer placement into a web can be controlled by the methods herein described to provide selective placement of the polymer within the web. Any additives and/or modifiers mixed into the polymer blend will likewise be selectively placed along with the polymer composition. The web is thereafter optionally cured to convert the curable composition into a solid elastomeric polymer.

The polymer composition is theorized to be caused to flow and distribute itself over fibers, cells or pores in a web under the influence of the processing conditions and apparatus provided by this invention. This flow and distribution is further theorized to be facilitated and promoted by the presence of a fluorochemical which has been preliminarily impregnated into a web, as taught herein. The amount of fluorochemical or fluorochemical residue in a web is believed to influence the amount, and the locations, where the polymer will collect and deposit, and produce encapsulated fibers and/or an internal layer in the web. However, there is no intent to be bound herein by theory.

Some portion of the residue of fluorochemical resulting from a preliminary web saturating operation is theorized to be present upon a treated fiber's surfaces after envelopment of fibers, cells or pores by the polymer has been achieved during the formation of the encapsulating fiber and/or the internal layer by the practice of this invention. This is believed to be demonstrated by the fact that a web treated by this invention still exhibits an enhanced water and oil repellency, such as is typical of fluorochemicals in porous webs. It is therefore believed that the fluorochemicals are affecting the adherence of the polymer as a thin film enveloping layer about the treated fibers, cells or pores as well as facilitating polymer pressurized flow within and about the interstices or open cells of the web being treated so that the polymer can assume its position enveloping the fibers or lining the cells or pores of the substrate.

In those fabrics that are pre-treated with fluorochemicals, the exact interrelationship between the polymer film and the impregnated fluorochemical is presently difficult, or perhaps impossible, to quantify because of the variables involved and because transparent polymer is difficult to observe by optical microscopy. It can be theorized that perhaps the polymer and the fluorochemical each tend to produce discontinuous films upon the fiber surface, and that such films are discontinuous in a complementary manner. It may alternatively be theorized that perhaps the polymer film is contiguous, or substantially so, relative to fluorochemical molecules on a fiber surface, and that the layer of polymer on a fiber surface is so thin that any dislodgement of the fluorochemical may release the fluorochemical into the polymer film thereby allowing the fluorine to orient or project through the film with the required cure temperature of the polymer, reactivating the water surface contact angle so that the water repellent properties of the fluorochemical affect the finished product. However, regardless of physical or chemical explanation, the combination of polymer film and fluorochemical results in a fiber envelopment or cell or pore wall lining and the formation of encapsulated fibers and/or an internal layer of polymer in a web when this invention is practiced. After curing, the polymer is permanently fixed material.

By using the methods of this invention, one can achieve a controlled placement of one or more additives and/or modifiers on and within the (a) thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) some combination of (a) and (b).

A curable polymer optionally mixed with one or more additives and/or modifiers is applied onto and into a tensioned web using compressive and shear forces. The extent of orienting additives and/or modifiers on and within the fiber envelopment and the cell or pore wall lining is believed to be regulatable. Regulating such orientation is accomplished by controlling the factors discussed previously, the selection and amount of fluorochemical, the type of polymer and additives (and/or modifiers) used, and the amount of compressive and shear forces employed at a given temperature. Such control ensures that fiber envelopment is achieved while the interstices and/or open cells of the web are not completely filled with such polymer in the region of the internal layer and that the outer opposed surfaces of the web are substantially completely free of polymer coating or residue. After such a procedure, the curable polymer is cured.

The curable polymer is optionally mixed with one or more additives and/or modifiers and then applied onto the surface of the web. Then the web, while tensioned, is passed over and against shearing means or through a compression zone, such as between rollers or against a shear knife. Thus, transversely applied shear force and compressive pressure is applied to the web. The combination of tension, shearing forces, and web speed is sufficient to cause the polymer composition to move into the web and out from the interstices or open cells around the web fibers, cells, or pores being enveloped. The result is that at least some of the interstices and/or open cells are unfilled in regions of the web outside of the region occupied by the internal coating or internal layer, and are preferably substantially free of polymer. Excess polymer is removed by the surface wiping action of the shearing means. The curable polymer enveloping the fibers is thereafter cured.

The desired penetration of, and distribution and placement of polymer and additives and/or modifier(s) in a web is believed to be achieved by localized pressuring forces exerted on a web surface which are sufficiently high to cause the viscosity of a polymer composition to be locally reduced, thereby permitting such polymer to flow under such pressuring and to be controllably placed within the web and to envelope its fibers or line the cell or pore walls thereof. To aid in this process, the web is preferably at least slightly distorted by tensioning or stretching, while being somewhat

transversely compressed at the location of the controlled placement. This distortion is believed to facilitate the entrance of the polymer composition into the web and the orientation of one or more additives and/or modifiers onto and into the web. When the compression and tension are released, the polymer composition is believed to be squeezed or compressed within and through the interstitial spaces, or open cell spaces, of the treated web.

If, for example, too much polymer is present in the finished product, then either or both the tension and shear force can be increased, and vice versa for too little polymer. If flow is not adequate upon the fibers, producing incomplete fiber envelopment, then the viscosity of the polymer composition can be reduced by increasing the pressures and/or temperatures employed for the controlled placement thereof. Alternatively, if the viscosity is too low, then the pressure and/or temperature can be decreased. If the polymer composition is resistant to being positioned or placed in a desired location in a desired amount in a given web at various viscosities and/or pressures, then the level of fluorochemical pretreatment of the web can be increased, or decreased, as the case may be. The above factors also influence the placement of additives and/or modifiers when the additives and/or modifiers are mixed into the polymer composition.

Some additives and/or modifiers, due to their physical and chemical properties, cannot be incorporated on and within a web by pre-treating the web or by mixing the additives and/or modifiers into the polymer composition. Such additives and/or modifiers can be topically applied to the web after the pressured, shear thinning stage described above, but before curing. Once topically applied, the additives and/or modifiers are forced into the web by passing through the exit nip rolls. The additives and/or modifiers will adhere to the polymer composition that forms encapsulated fibers, an internal layer, or some combination of the above. Some additives and/or modifiers may even adhere to the structural elements of the web.

As indicated above, the activity transpiring at a final step in the practice of this invention is generically referred to as curing. Conventional curing conditions known in the prior art for curing polymer compositions are generally suitable for use in the practice of this invention. Thus, temperatures in the range of about 250° F. to about 350° F. are used and times in the range of about 30 seconds to about 1 minute can be used, although longer and shorter curing times and temperatures may be used, if desired, when thermal curing is practiced. Radiation curing, as with an electron beam or ultraviolet light, can also be used. However, using platinum catalysts to accelerate the cure while using lower temperatures and shorter cure times is preferable.

Since either filled, plugged, almost filled interstices, or open cells in the region of an internal layer remain transmissive of air in cured webs made by this invention, the webs are characteristically air permeable or breathable.

Sample webs or fabrics that are beneficially treated, fiber enveloped and internally coated in accordance with the invention include nylon, cotton, rayon and acrylic fabrics, as well as fabrics that are blends of fiber types. Sample nylon fabrics include lime ice, hot coral, raspberry pulp, and diva blue Tactel® (registered trademark of ICI Americas, Inc.) fabrics available from agent Arthur Kahn, Inc. Sample cotton fabrics include Intrepid® cotton cornsilk, sagebrush cotton, and light blue cotton fabrics available also from Arthur Kahn, Inc. Non-woven, monofilamentous, fabrics such as TYVEK® (registered trademark of E.I. duPont de Nemours Co., Inc.) and the like are also employable. It is believed that when sufficient energy is introduced that some portion of the durable water repellent finish is removed from the pretreated web and blooms to the surface of the polymer if the polymer thin film is sufficiently thin and the viscosity and rheology is modified sufficiently during the shear thinning process step of the invention.

As indicated above, a web is preferably pretreated and impregnated with a fluorochemical prior to being treated with a polymer composition as taught herein. The fluorochemical impregnation is preferably accomplished by first saturating a web with a liquid composition which incorporates the fluorochemical, and then, thereafter, removing the excess liquid composition and residual carrier fluid by draining, compression, drying, or some combination thereof from the treated web.

It is now believed that any fluorochemical known in the art for use in a web, particularly fabric treatment in order to achieve water repellency, soil repellency, grease repellency, or the like, can be used for purposes of practicing the present invention. It is believed that a typical fluorochemical of the type used for web treatment can be characterized as a compound having one or more highly fluorinated portions, each portion being a fluoroaliphatic radical or the like, that is (or are) functionally associated with at least one generally non-fluorinated organic portion. Such organic portion can be part of a polymer, part of a reactive monomer, a moiety with a reactable site adapted to react with a binder, or the like. Such a compound is typically applied to a fabric or other web as a suspension or solution in either aqueous or non-aqueous media. Such application may be conventionally carried out in combination with a non-fluorine or fluorine containing resin or binder material for the purpose of providing improved durability as regards such factors as laundering, dry cleaning, and the like.

Fluorochemicals are sometimes known in the art as durable water repellent (DWR) chemicals, although such materials are typically believed to be not particularly durable and to have a tendency to wash out from a fabric treated therewith. In contrast, fiber enveloped webs of this invention which have been pretreated with a fluorochemical display excellent durability and washability characteristics. Indeed, the combination of fluorochemical pretreatment and silicone polymer fiber envelopment such as provided by the present invention appears to provide synergistic property enhancement because the effects or properties obtained appear to be better than can be obtained by using either the fluorochemical or the silicone polymer alone for web treatment.

Exemplary water repellent fluorochemical compositions include the compositions sold under the name Milease® by ICI Americas Inc. with the type designations F-14N, F-34, F-31X, F-53. Those compositions with the "F" prefix indicate that they contain a fluorochemical as the principal active ingredient. More particularly, Milease® F-14 fluorochemical, for example, is said to contain approximately 18 percent perfluoroacrylate copolymer, 10 percent ethylene glycol (CAS 107-21-1) and 7 percent acetone (CAS 67-64-1) dispersed and dissolved in 65 percent water. Milease® F-31X is said to be a dispersion of a combination of fluorinated resin, acetone, and water.

Still another suitable class of water repellent chemicals is the Phobotex® chemicals of Ciba/Geigy identified as Phobotex® FC104, FC461, FC731, FC208 and FC232 which are each believed to be suitable for use, typically in approximately a 5 percent concentration, in saturating a web for use in the invention. These and many other water repellent fluorochemicals are believed to be capable of creating a surface contact angle with water of greater than about 90 degrees when saturated into a web and to be suitable for use in the practice of this invention.

Another group of useful water repellent fluorochemicals is the TEFLON® -based soil and stain repellents of E. I. duPont de Nemours & Co. Inc., 1007 Market Street, Wilmington, Del. 19898. Suitable TEFLON® types for use in the practice of this invention include TEFLON® G. NPA, SKF, UP, UPH, PPR, N and MLV. The active water repellent chemical of each composition is believed to be a fluorochemical in polymeric form that is suitable for dispersion in water, particularly in combination with a cationic surfactant as a dispersant. These dispersions are dilutable in all proportions with water at room temperature. One preferred class of fluorochemical treating compositions useful in the practice of this invention comprises about 1 to about 10 weight percent, more preferably about 5 weight percent of one of the above indicated TEFLON®-type water repellent fluorochemicals in water.

Another major group of suitable water repellent fluorochemical compositions useful in the practice of the invention is commercially available under the designation ZEPEL® rain and stain repellent chemicals of E. I. duPont de Nemours & Co. Inc., such as ZEPEL® water repellent chemicals types B, D, K, RN, RC, OR, HT, 6700 and 7040. Each is believed to be a fluorochemical in polymeric form that is dispersible in all proportions at room temperature. The dispersants ZEPEL® B, D, K, and RN are believed to be cationic, while the dispersant ZEPEL® RC is believed to be nonionic.

As an exemplary composition, ZEPEL® 6700 is said to be comprised of 15 to 20 percent perfluoroalklyl acrylic copolymer, 1 to 2 percent alkoxylated carboxylic acid, and 3 to 5 percent ethylene glycol. Exemplary characteristics of the composition include a boiling point of 100° C. at 760 mm Hg and a specific gravity of 1.08. The volatiles are approximately 80 percent by weight. The pH is 2 to 5. The odor is mild; the concentrate form is that of a semi-opaque liquid; and the concentrate color is straw white. The composition and characteristics of ZEPEL® 7040 repellent chemical are believed to be substantially identical to those of ZEPEL® 6700 except that the former composition additionally contains 7 to 8 percent acetone.

Another major group of water repellent fluorochemicals comprises the Scotchgard® water repellent chemicals of 3M Co., St. Paul, Minn. The Scotchgard® fluorochemicals are believed to be aqueously dispersed fluorochemicals in polymeric form. The compositions of two suitable Scotchgard® water repellent fluorochemicals are believed to be disclosed in U.S. Pat. Nos. 3,393,186 and 3,356,628, which patents are incorporated herein by reference. Thus, the Scotchgard® fluorochemical of U.S. Pat. No. 3,356,628 consists of copolymers of perfluoroacrylates and hydroxyalkyl acrylates. These copolymers are suitable for use as an oil and water repellent coating on a fibrous or porous surface. They have a carbon to carbon main chain and contain recurring monovalent perfluorocarbon groups having from 4 to 18 carbon atoms each and also having recurring hydroxyl radicals. From 20 to 70 percent of the weight of such copolymer is contributed by fluorine atoms in the perfluorocarbon groups and from 0.05 to 2 percent of the weight of the copolymer is contributed by the hydroxyl radicals. Such copolymer is said to have improved surface adherability properties as compared to the homopolymer of a corresponding fluorocarbon monomer.

The Scotchgard® fluorochemical of U.S. Pat. No. 3,393,186 consists of perfluoroalkenylacrylates and polymers thereof. An exemplary fluorinated monomer has the formula:

$$R_fCH{=}CH(CH_2)_nO{-}\overset{O}{\overset{\|}{C}}{-}\overset{R}{\overset{|}{C}}{=}CH_2$$

Wherein R_f is a fluorocarbon group having from 3 to 18 carbon atoms, R is hydrogen or methyl, and n is 0–16. Such a water repellent fluorochemical composition is supplied and saturated into the substrate web as a readily pourable aqueous dispersion.

U.S. Pat. No. 4,426,476 discloses a fluorochemical textile treating composition containing a water-insoluble fluoroaliphatic radical, an aliphatic chlorine-containing ester and a water insoluble, fluoroaliphatic radical containing polymer.

U.S. Pat. No. 3,896,251 discloses a fluorochemical textile treating composition containing a fluoroaliphatic radical containing linear vinyl polymer having 10 to 60 weight percent fluorine and a solvent soluble carbodiimide preferably comprising fluoroaliphatic groups. A table in this patent lists a plurality of prior art fluoroaliphatic radical containing polymers useful for the treatment of fabrics and the prior art patents where such polymers are taught.

U.S. Pat. No. 3,328,661 discloses textile treating solutions of a copolymer of an ethylenically unsaturated fluorocarbon monomer and a ethylenically unsaturated epoxy group containing monomer.

U.S. Pat. No. 3,398,182 discloses fluorocarbon compounds useful for fabric treatment that contain a highly fluorinated oleophobic and hydrophobic terminal portion and a different nonfluorinated oleophilic portion linked together by a urethane radical.

Water repellent fluorochemical compositions are preferably utilized to saturate a starting untreated porous web substrate so that such composition and its constituents wet substantially completely and substantially uniformly all portions of the web. Such a saturation can be accomplished by various well known techniques, such as dipping the web into a bath of the composition, or padding the composition onto and into the web, or the like. Padding is the presently preferred method of fluorochemical application.

After application of the fluorochemical composition to the web, the water (or liquid barrier) and other volatile components of the composition are removed by conventional techniques to provide a treated web that contains the impregnated fluorochemical throughout the web substrate.

In a preferred procedure of fluorochemical controlled placement, a web is substantially completely saturated with an aqueous dispersion of a fluorochemical. Thereafter, the resulting impregnated web is compressed to remove excess portions of said dispersion. Finally, the web is heated to evaporate the carrier liquid. If the fluorochemical is curable, then the heating also accomplishes curing. After the fluorochemical treatment, the fluorochemical is found only on or in the web structural elements or fibers and is substantially completely absent from the web interstices.

The fluorochemical concentration in the treating composition is such as to permit a treated fluorochemical containing web, after volatiles of the treating composition are removed, to exhibit a contact angle with water applied to an outer web surface which is greater than about 90°. More preferably, the contact angle provided is greater than about 130°.

The web weight add-on provided by the fluorochemical after removal of volatiles is usually relatively minor. However, the weight add on can vary with such factors as the nature of web treated, the type of polymer composition utilized in the next step of the process, the temperature at which the composition is applied, the ultimate use contemplated for a web, and the like.

Typical weight add-ons of fluorochemical are in the range of about 1 to about 10 percent of the original weight of the web. More preferably, such weight add-ons are about 2 to about 4 weight percent of the weight of the starting fabric.

Durability of a web that has been treated with a fluorochemical and durability of a web that is subsequently treated with a polymer can sometimes be improved by the conventional process of "sintering". The exact physical and chemical processes that occur during sintering are unknown. The so-called sintering temperature utilized is a function of the fluorochemical composition utilized and such temperature is frequently recommended by fluorochemical manufacturers. Typically, sintering is carried out at a temperature of about 130° to about 160° C. for a period of time of about 2 to about 5 minutes. Acid catalysts can be added to give improved durability to laundering and dry cleaning solvents.

The fluorochemical is believed to provide more than water or other repellent properties to the resulting treated web, particularly since the curable polymer is often itself a water repellent. Rather, and without wishing to be bound by theory, it is believed that the fluorochemical in a treated web provides relative lubricity for the treated fibers during the pressure application of the curable polymer. The polymer is applied under pressures which can be relatively high, and the polymer is itself relatively viscous, as is discussed herein. In order for the curable polymer to coat and envelop web fibers, but not fill web interstitial individual filament or fiber voids, the fibers of the web may move over and against each other to a limited extent, thereby to permit entry of the polymer into and around the fibers. It is thought that the fluorochemical deposits may facilitate such fiber motion and facilitate envelopment during the pressure application and subsequent shearing processing.

Alternatively, the fluorochemical may inhibit deposition of the polymer at the positions of the fluorochemical deposits which somehow ultimately tends to cause this enveloping layers of polymer to form on fibers.

The precise physics and chemistry of the interaction between the fluorochemical and the polymer is not understood. A simple experiment demonstrates movement of the liquid polymer as influenced by the presence of the fluorochemical:

A piece of fabric, for example the Red Kap Milliken poplin polyester cotton blend fabric, is cut into swatches. One swatch is treated with an adjuvant, for example a three percent solution of the durable water-repellent chemical Milease® F-31X. The treated swatch and an untreated swatch are each positioned at a 45° angle to plumb. A measured amount, for example one-half ounce, of a viscous polymer composition, for example the Mobay® 2530A/B silicon composition, is dropped onto the inclined surface of each swatch. The distance in centimeters that the composition flows downwards upon the surface of the swatch is measured over time, typically for 30 minutes.

A graphical plot of the flow of the silicone composition respectively upon the untreated and treated swatches is shown in FIG. 1. At the expiration of 30 minutes the viscous composition has typically traveled a distance of about 8.8 centimeters upon the treated swatch, or a rate of about 0.29 centimeters per minute. At the expiration of the same 30 minutes, the viscous composition has typically traveled a lesser distance of about 7.1 centimeters upon the untreated swatch, or a rate of about 0.24 centimeters per minute.

Qualitatively commensurate results are obtainable with other DWR fluorochemical adjuvants that facilitate the viscous flow of polymer compositions in accordance with the invention. Indeed, if desired, the simple flow rate test can be used to qualify an adjuvant compound for its employment within the method of the invention. The fluorochemical pre-treated web generally increases the surface contact angle of the polymer while reducing the amount of saturation of the polymer into the fibers themselves.

The fluorochemical treated web is thereafter treated under pressure with a predetermined amount of a curable polymer composition and one or more additives and/or modifiers optionally mixed into the polymer composition, to form a web whose fibers are preferably substantially completely enveloped with such curable polymer and whose outer surfaces and interstices are preferably substantially completely free of the curable polymer. The polymer is thereafter cured by heat, radiation, or the like. Even room temperature curing can be used. A polymer impregnated, fluorochemical pretreated web can be interveningly stored before being subjected to curing conditions depending upon the storage or shelf life of the treating silicone polymer composition.

A curable polymer composition utilized in the practice of this invention preferably has a viscosity that is sufficient to achieve an internal coating of the web. Generally, the starting viscosity is greater than about 1000 centipoise and less than about 2,000,000 centipoise at a shear rate of 10 reciprocal seconds. It is presently most preferred that such composition have a starting viscosity in the range of about 5,000 to about 1,000,000 centipoise at 25° C. Such a composition is believed to contain less than about 1% by weight of volatile material.

The polymer is believed to be typically polymeric and to be commonly a mixture of co-curable polymers, oligomers, and/or monomers. A catalyst is usually also present, and, for the presently preferred silicone polymer compositions discussed hereinafter, is platinum or a platinum compound, such as a platinum salt.

A preferred class of liquid curable silicone polymer compositions comprises a curable mixture of the following components:

(A) at least one organo-hydrosilane polymer (including copolymers);

(B) at least one vinyl substituted polysiloxane (including copolymers);

(C) a platinum or platinum containing catalyst; and

(D) (optionally) fillers and additives.

Typical silicone hydrides (component A) are polymethylhydrosiloxanes which are dimethyl siloxane copolymers. Typical vinyl terminated siloxanes are vinyldimethyl terminated or vinyl substituted polydimethylsiloxanes. Typical catalyst systems include solutions or complexes of chloroplatinic acid in alcohols, ethers, divinylsiloxanes, and cyclic vinyl siloxanes.

The polymethylhydrosiloxanes (component A) are used in the form of their dimethyl copolymers because their reactivity is more controllable than that of the homopolymers and because they result in tougher polymers with a lower cross-link density. Although the reaction with vinyl functional silicones (component B) does reportedly take place in 1:1 stoichiometry, the minimum ratio of hydride (component A) to vinyl (component B) in commercial products is reportedly about 2:1 and may be as high as 6:1. While the hydrosilation reaction of polymethylhydrosilane is used in both so called RTV (room temperature vulcanizable) and LTV (low temperature vulcanizable) systems, and while both such systems are believed to be useful in the practice of the present invention, systems which undergo curing at elevated temperature are presently preferred.

Particulate fillers are known to be useful additives for incorporation into liquid silicone polymer compositions.

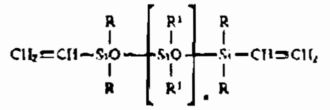
Such fillers apparently not only can extend and reinforce the cured compositions produced therefrom, but also can favorably influence thixotropic behavior in such compositions. Thixotropic behavior is presently preferred in compositions used in the practice of this invention. A terminal silanol (Si—OH) group makes such silanol siloxanes susceptible to reaction in curing, as is believed desirable.

It is believed that all or a part of component B can be replaced with a so called silanol vinyl terminated polysiloxane while using an organotin compound as a suitable curing catalyst as is disclosed in U.S. Pat. No. 4,162,356. However, it is presently preferred to use vinyl substituted polysiloxanes in component B.

A polymer composition useful in this invention can contain curable silicone resin, curable polyurethane, curable fluorosilicone, curable modified polyurethane silicones, curable modified silicone polyurethanes, curable acrylics, polytetrafluoroethylene, and the like, either alone or in combination with one or more compositions.

One particular type of silicone composition which is believed to be well suited for use in the controlled placement step of the method of the invention is taught in U.S. Pat. Nos. 4,472,470 and 4,500,584 and in U.S. Pat. No. 4,666,765. The contents of these patents are incorporated herein by reference. Such a composition comprises in combination:

(i) a liquid vinyl chain-terminated polysiloxane having the formula.



wherein R and R^1 are monovalent hydrocarbon radicals free of aliphatic unsaturation with at least 50 mole percent of the R^1 groups being methyl, and where n has a value sufficient to provide a viscosity of about 500 centipoise to about 2,000,000 centipoise at 25° C.;

(ii) a resinous organopolysiloxane copolymer comprising:
  (a) $(R^2)_3SiO_{0.5}$ units and SiO_2 units, or
  (b) $(R^3)_2SiO_{0.5}$ units, $(R^3)_2SiO$ units and SiO_2 units, or
  (c) mixtures thereof, where R^2 and R^3 are selected from the group consisting of vinyl radicals and monovalent hydrocarbon radicals free of aliphatic unsaturation, where from about 1.5 to about 10 mole percent of the silicon atoms contain silicon-bonded vinyl groups, where the ratio of monofunctional units to tetrafunctional units is from about 0.5:1 to about 1:1, and the ratios of difunctional units to tetrafunctional units ranges up to about 0.1:1:

(iii) a platinum or platinum containing catalyst; and

(iv) a liquid organohydrogenpolysiloxane having the formula:

$$(R)_a(H)_bSiO_{\frac{4-a-b}{2}}$$

in an amount sufficient to provide from about 0.5 to about 1.0 silicon-bonded hydrogen atoms per silicon-bonded vinyl group of above component (i) or above subcomponent (iii) of, R_- is a monovalent hydrocarbon radical free of aliphatic unsaturation, and has a value of from about 1.0 to about 2.1, b has a value of from about 0.1 to about 1.0, and the sum of a and b is from about 2.0 to about 2.7, there being at least two silicon-bonded hydrogen atoms per molecule.

Optionally, such a composition can contain a finely divided inorganic filler (identified herein for convenience as component (v)). Also, such a composition can optionally contain one or more additives and/or modifiers (identified herein as component (vi)).

For example, such a composition can comprise on a parts by weight basis:

(a) 100 parts of above component (i);

(b) 100–200 parts of above component (ii);

(c) a catalytically effective amount of above component (iii), which, for present illustration purposes, can range from about 0.01 to about 3 parts of component (iii), although larger and smaller amounts can be employed without departing from operability (composition curability) as those skilled in the art will appreciate;

(d) 50–100 parts of above component (iv), although larger and smaller amounts can be employed without departing from operability (curability) as those skilled in the art will appreciate;

(e) 0–50 parts of above component (v); and

(f) variable amounts of above component (vi) depending on the component and the exact functionality desired, as one skilled in the art will appreciate.

Embodiments of such starting composition are believed to be available commercially from various manufacturers under various trademarks and trade names, with the exception of the addition of various additives and/or modifiers discussed in this invention.

As commercially available, such a composition is commonly in the two-package form (which are combined before use). Typically, the component (iv) above is maintained apart from the components (i) and (ii) to prevent possible gelation in storage before use, as those skilled in the art appreciate. For example, one package can comprise components (i) and (ii) which can be formulated together with at least some of component (ii) being dissolved in the component (i), along with component (iii) and some or all of component (v) (if employed), while the second package can comprise component (iv) and optionally a portion of component (v) (if employed). By adjusting the amount of component (i) and filler component (v) (if used) in the second package, the quantity of catalyst component (iii) required to produce a desired curable composition is achieved. Preferably, component (iii) and the component (iv) are not included together in the same package. As is taught, for example, in U.S. Pat. No. 3,436,366 (which is incorporated herein by reference), the distribution of the components between the two packages is preferably such that from about 0.1 to 1 part by weight of the second package is employed per part of the first package. For use, the two packages are merely mixed together in suitable fashion at the point of use. Component (vi) is optionally mixed into the polymer composition just prior to applying to a porous web.

Other suitable silicone polymer compositions, without additives, are disclosed in the following U.S. patents:

U.S. Pat. No. 4,032,502 provide compositions containing a linear polydiorganosiloxane having two siloxane bonded vinyl groups per molecule, organosiloxane that is soluble in such linear polydiorganosiloxane and comprised of a mixture of a polyorganosiloxane and a polydiorganosiloxane, platinum-containing catalyst, a platinum catalyst inhibitor, and a reinforcing silica filler whose surface has been treated with an organosilicone compound.

U.S. Pat. No. 4,108,825 discloses a composition comprising a triorganosiloxy end-blocked

polydiorganosiloxane, an organohydrogensiloxane having an average of at least 2.1 silicon-bonded hydrogen atoms per molecule, a reinforcing silica filler having a surface treated with an organosilicone compound, a platinum catalyst, and ceric hydrate. Such silicone polymer composition is desirable when a web is being prepared which has flame retardant properties.

U.S. Pat. No. 4,162,243 discloses a silicone composition of 100 parts by weight triorganosiloxy end-blocked polydimethylsiloxane, reinforcing amorphous silica that is surface treated with organosiloxane groups, organohydrogensiloxane, and platinum catalyst.

U.S. Pat. No. 4,250,075 discloses a liquid silicone polymer composition that comprises vinyldiorganosiloxy end-blocked polydiorganosiloxane, polyorganohydrogensiloxane, platinum catalyst, platinum catalyst inhibitor, and carbonaceous particles. Such a silicone polymer composition is useful when a web of this invention is being prepared that has electrically conductive properties.

U.S. Pat. No. 4,427,801 discloses a curable organopolysiloxane of liquid triorganosiloxy end-blocked polydiorganosiloxane wherein the triorganosiloxy groups are vinyl dimethylsiloxy or vinylmethylphenylsiloxy, finely divided amorphous silica particles treated with mixed trimethylsiloxy groups and vinyl-containing siloxy groups, organopolysiloxane resin containing vinyl groups, organohydrogensiloxane, and a platinum containing catalyst.

U.S. Pat. No. 4,500,659 discloses a silicone composition of liquid triorganosiloxy end-blocked polydimethylsiloxane wherein the triorganosiloxy units are dimethylvinylsiloxy or methylphenylvinylsiloxy, a reinforcing filler whose surface has been treated with a liquid hydroxyl end-blocked polyorganosiloxane which is fluorine-substituted, a liquid methylhydrogensiloxane, and a platinum-containing catalyst.

U.S. Pat. No. 4,585,830 discloses an organosiloxane composition of a triorganosiloxy end-blocked polydiorganosiloxane containing at least two vinyl radicals per molecule, an organohydrogensiloxane containing at least two silicone-bonded hydrogen atoms per molecule, a platinum-containing hydrosilation catalyst, optionally a catalyst inhibitor, a finely divided silica filler and a silica treating agent which is at least partially immiscible with said polydiorganosiloxane.

U.S. Pat. No. 4,753,978 discloses an organosiloxane composition of a first diorganovinylsiloxy terminated polydiorganosiloxane exhibiting a specified viscosity and having no ethylenically unsaturated hydrocarbon radicals bonded to non-terminal silicon atoms, a second diorganovinylsiloxy terminated polydiorganosiloxane that is miscible with the first polydiorganosiloxane and contains a vinyl radical, an organohydrogensiloxane, a platinum hydrosilation catalyst, and a treated reinforcing silica filler.

U.S. Pat. No. 4,785,047 discloses silicone elastomers having a mixture of a liquid polydiorganosiloxane containing at least two vinyl or other ethylenically unsaturated radicals per molecule and a finely divided silica filler treated with a hexaorganodisilazane which mixture is then compounded with additional hexaorganodisiloxane.

U.S. Pat. No. 4,329,274 discloses viscous liquid silicone polymer compositions that are believed to be suitable and which are comprised of vinyl containing diorganopolysiloxane (corresponding to component B), silicon hydride siloxane (corresponding to component A) and an effective amount of a catalyst which is a halogenated tetrameric platinum complex.

U.S. Pat. No. 4,442,060 discloses a mixture of 100 parts by weight of a viscous diorganopolysiloxane oil, 10 to 75 parts by weight of finely divided reinforcing silica, 1 to 20 parts by weight of a structuring inhibitor, and 0.1 to 4 parts by weight of 2,4-dichlorobenzoyl peroxide controlled cross-linking agent.

Silicone resin compositions shown in Table I below have all been used in the practice of this invention. Such compositions of Table I are believed to involve formulations that are of the type hereinbove characterized.

TABLE I

Illustrative Starting Polymer Compositions

MANUFACTURER	TRADE DESIGNATION	COMPONENTS[1]
Mobay	Silopren ® LSR 2530	Vinyl-terminated polydimethylsiloxane with fumed silica, methylhydrogen polysiloxane
Mobay	Silopren ® LSR 2540/01	
Dow Corning	Silastic ® 595 LSR	Polysiloxane
Dow Corning	2303	Polysiloxane
Dow Corning	2962	Polysiloxane
General Electric	SLE 5100	Polysiloxane
General Electric	SLE 5106	Siloxane resin solution
General Electric	SLE 5110	Polysiloxane
General Electric	SLE 5300	Polysiloxane
General Electric	SLE 5500	Polysiloxane
General Electric	SLE 6108	Polysiloxane
Shin-Etsu	KE 1917	
Shin-Etsu	DI 1940-30	
SWS Silicones Corporation	Liquid Rubber BC-10	Silicone fluid with silicone dioxide filler and curing agents

Table I footnote:
[1] Identified components do not represent complete composition of the individual products shown.

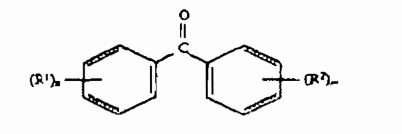
When a polymer composition of a silicone polymer and a benzophenone is pressured into a porous web as taught herein, protection of an organic web against ultraviolet radiation is improved, and the degradation effects associated with ultraviolet light exposure are inhibited, as may be expected from prior art teachings concerning the behavior of benzophenones.

Ultra-violet-absorbing agents contemplated for use in the practice of the present invention include uvA absorbers such as benzophenone-8-methyl anthranilate; benzophenone-4; benzophenone-3; 2,4-dihydroxy-benzophenone; uvB absorbers such as p-aminobenzoic acid (PABA); pentyl dimethyl PABA; cinoxate; DEA p-methoxycinnamate, digalloyl trioleate; ethyl dihydroxypropyl PABA; octocrylene, octyl methoxycinnamate, oleyl salicylate, glyceryl PABA; homosalate; lawsone plus dihydroxyacetone; octyl dimethyl PABA; 2-phenylbenzimidazole-5-sulfonic acid; TEA salicylate; sulfomethyl benzylidene bornanone; urocanic acid and its esters, and physical barriers such as red petrolatum and titanium dioxide.

To prepare a silicone polymer composition which incorporates a benzophenone, one preferably admixes the benzophenone with the silicone polymer composition at the time of use. The benzophenone component can be regarded as, or identified herein for convenience as the modifier component (vi). On the same parts by weight basis above used, a composition of this invention contains from about 0.1 to about 15 parts of component (vi), although the

preferred amount is from about 0.3 to about 10 parts of component (vi) and smaller amounts can be used, if desired, without departing from the spirit and scope of the invention.

One class of derivatized benzophenones useful in the practice of this invention is characterized by the generic formula:



where,

R^1 and R^2 are each selected from the group consisting of hydroxyl, lower alkoxy, and hydrogen, and n and m are each an integer of 1 or 2. Examples of substituted benones of the above formula include the substances shown below.

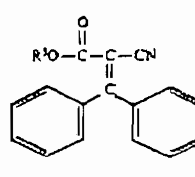
TABLE II

Substituted Benzophenones

ID NO.	NAME	COMMERCIALLY AVAILABLE UNDER SPECIFIED TRADEMARK FROM BASF
1	2,4-dihydroxybenzophenone	"Uvinul" 400[1]
2	2-hydroxy-4-methoxy-benzophenone	"Uvinul" M-40
3	2,2',4,4'-tetrahydroxybenzophenone	"Uvinul" D-50
4	2,2'-dihydroxy-4,4'-dimethoxy-benzophenone	"Uvinul" D-49
5	Mixed tetra-substituted benzophenones	"Uvinul" 490

Table II footnote:
[1]Presently most desired substituted benzophenone

Another class of derivatized benzophenones useful in the practice of this invention is characterized by the generic formula:



where R^3 is a lower alkyl radical.

An example of a substituted benzophenone of the previous formula is: 2-ethylhexyl-2-cyano3,3-diphenylacrylate (available from BASF under the trademark "Uvinul N-539").

In the last two formulas, the term "lower" refers to a radical containing less than about 8 carbon atoms.

The contact angle exhibited by a silicone composition used in this invention varies with the particular web which is to be saturated therewith. However, the contact angle of water is generally lower for the non-treated side than the treated side. A combination of the processed web, the silicone polymer and the fluorochemical generally produces higher water contact angles than webs treated only with fluorochemicals. The performance of a polymer composition may be determined by the nature of a previously applied saturant such as a fluorochemical. Suitable starting compositions include 100% liquid curable silicone rubber compositions, such as SLE5600 A/B from General Electric, Mobay LSR 2580A/B, Dow Corning Silastic® 595 LSR and Silastic® 590 which when formulated with substituted benzophenone as taught herein will form a contact angle of much greater than 70 degrees, and typically of 90+ degrees, with typical porous webs (such as fabrics) that have a residue of fluorochemical upon (and within) the web from a prior saturation.

The polymer composition used in the practice of this invention can also carry additives into the three-dimensional structure of the web during the pressured application. Further, it is preferable, that any additive s and/or modifiers be bound into the cured composition permanently as located in the three-dimensional structure of the web. Particularly in the case of fabrics, this desirably positions the additives and/or modifiers mainly on surface portions of the encapsulated yarns and fibers in positions where they typically are beneficially located and maintained, or on the surfaces of the internal layer, or on the surfaces of the web, or some combination thereof. When necessary, the polymer composition, the fabric used, and the particular additive and/or modifier compounds can be altered to create specific functional properties such as adhesiveness, antimicrobial activity, blood repellency, conductivity, fire resistance, flexibility, good hand, stain resistance, ultraviolet absorption capabilities, and other functions described by this invention.

Silicone polymers, when compounded with additives and/or modifiers, produce desirable properties. For example, a fine particle silica is added to silicone polymer as a filler or reinforcing agent to increase the hardness and reduce the stickiness. Carbon black is added when electrical conductivity is required. Red iron oxide improves heat resistance. Zinc oxide is used for heat conductivity. Aluminum hydrate is added for extra electrical track resistance. Various pigments are used for coloring. Such solid additives and/or modifiers can be added by mixing with silicone polymer at a certain ratio. Mixing of the silicone polymer is usually performed by a mixer, or the like. Care should be taken to add the additive (and/or modifier) powders slowly enough to prevent balls of high additive and low silicone content from forming and floating on top of the silicone polymer which leads to poor dispersion. Poor dispersion will result in an uneven distribution of the additive and/or modifier on and within the web. If much additive and/or modifier is being added, several separate additions and cross blending between them will assure good dispersion. The sequence of addition is also important. For instance, when extending fillers are added, they should be added after the reinforcing fillers. Color, when used, may be added at this stage. The catalyst is added at the final stage or is part of the co-blended polymer composition. Care should be taken to be sure the compound temperature is cool enough to prevent unexpected curing of the silicone polymer.

Liquid additives and/or modifiers can be added by directly mixing with silicone polymer or finely dispersing in the silicone polymer. Additives and/or modifiers can also be added in a homogeneous form such as dissolving in suitable organic solvents or water, or in a heterogeneous form such as latex. For example, hydrophobic polyurethanes or fluorocarbon polymers can be dispersed in water by addition of emulsifiers or surfactants in a emulsion form or latex.

A wide variety of additives, agents, or modifiers, herein used interchangeably, can be used in accordance with the practice of this invention to produce porous webs that retain the functional properties of the agents incorporated within the web. It is impossible to list in certainty all of the agents and modifiers that can be used in accordance with the practice of the present invention. Many of the additives used in the plastics industry are described in handbooks and can

be used in accordance with the practice of this invention. Two such handbooks are *Plastics Additives: An Industrial Guide*, by Ernest W. Flick (Noyes Publications 1986), and *Chemical Additives For The Plastics Industry: Properties, Applications, Toxicologies*, by the Radian Corporation (Noyes Data Corp. 1987), herein incorporated by reference. The charts below list (1) additives known to work in accordance with the practice of this invention, (2) additives that are substantially similar in physical and/or chemical properties to the additives that are known to work in accordance with the practice of this invention, and (3) additives that were unknown in the art as of the printing of the above referenced handbooks. Some of these agents are discussed in greater detail in subsequent sections.

Adhesive Agents

Epoxy-resin
Co-oligomer
Phenolic resins
Polyurea resins
Polyolefins
Polyamides
Polysiloxanes
Polysulfides
Polyvinyl esters
Neoprene
Polyurethanes
Polyacetal resin, with one or more members selected from the group consisting of isocyanate and isothiocyanate compounds.

Anti-Static Agents

Fatty acid esters and their derivatives
Long-chain amines
Amides
Quaternary ammonium salts
Polyoxyethylene derivatives
Polyhydric alcohols and their derivatives
1,2-epoxides such as 1,2-epoxyhexane, 1,2-epoxyoctane, 1,2-epoxynonane, 1,2-epoxydecane, 1,2-epoxydodecane, 7,8-epoxyoctadecane, 9,10-epoxyoctadecane, 5,6-epoxydodecane, 7,8-epoxyoctadecane, 2,3-epoxydodecane, 5,6-epoxydodecane, 7,8-epoxyoctadecane, 9,10-epoxyoctadecane, 10,11-epoxyeicosane.
Epoxides reacted under acid or alkaline catalyst conditions with ethylene glycols or 1,2-propylene glycols. Example catalysts are BF etherate, sulfuric acid, sodium methylate, and lithium methylate. Preferable ethylene or propylene glycols are mono-, di, tri and tetra.

Biocidal Agents

Halogens and halogen based compounds such as iodine, chloroazodin, chlorinated cyanuric acid derivatives, and chloramine derivatives.
Antibiotics
Anti-virals such as zidovudine
Nonoxynol-9
Phenols and phenolic compounds such as o-phenylphenol, o-benzyl-p-chlorophenol, p-tert-amylphenol, bisphenols such as hexachlorophene, dichlorophene, methylene-bis(4-chlorophenol), fentichlor, and triclosan.
Quaternary ammonium salts such as cetrimide, benzalkonium chloride, cetylpyridinium chloride, laurolinium acetate, dequalinium chloride, hedaquinium chloride, polyquaternium 1
Zinc oxide, 2-N-octyl-4-isothiazole-3-one
Phenyl mercuric acetate
Skin disinfectants such as alcohols, mercurials, silver compounds, neomycin
Water disinfectants such as chlorine and sodium hypochlorite
Air disinfectants such as propylene glycol, lactic acid, glycolic acid, and levulinic acid
Gaseous disinfectants such as ethylene oxide, β-propiolactone, and formaldehyde
Clothing disinfectants such as neomycin
Methyl dimethyl propoxylene ammonium chloride
Polyiodide material like Pentaiodid
Acid salts derived from hydrochloric, methane sulfonic, ethanesulfonic, isothionic, lactic, and citric acids
Trichlorocarbon

-continued

Blood Repellents

Antimicrobial or biocidal agents
Monoaldehyde
Iodophors such as povidone-iodine, polyvinyl pyrrolidone (PVP) or povidone USP, butyl cellosolve albumin-povidone-iodine complex
Polyethylene glycol mono (nonylphenyl) ether
Diethyl ether
Phenol resin
Urea resin
Urethane modified epoxy resin
Organosilicon quaternary ammonium salts

Dyes and Pigments

Azoic dyes
Cationic Dyes
Sulfur dyes
Nigrosine
Carbon black

Electrical Conductive Agents

Metal particles or fillers
Zinc oxide
Stannic oxide
Indium oxide
Tungsten and tungsten carbide
Carbon black
Graphite and metal coated graphite
Conductive polymers
Silver, nickel, copper, aluminum, gold
Rhodium
Ruthenium
Molybdenum
Iridium
Platinum
Palladium

Electromagnetic Shielding Agents

Hypophosphorous
Carbon-phenol resin compound

Fillers

Carbon
Molecular sieves
Fumed silica
Colloidal silica

Flame Retardant Agents

Aluminum hydroxide
Borax
Tetrakis (hydroxymethyl)
Phosphonium chloride
Potassium hexafluoro zirconate
Potassium hexafluoro titanate
Polyamide
Polyamide
Poly-parabanic acid
Polyether sulfone, polyether ether keton, polyetherimide
Fluoroplastic resin films
Plyphenylene sulfide
Magnesium hydroxide
Silicone treated magnesium oxide
Polybenzimidazole
Non-flame durable fibers with flame durable fibers of metal such as stainless steel, copper, nickel
Carbon or carbonizable compositions
Kevlar ™
Nomex ™
Retardant powder fillers such as alumina trihydrate
Kaolin, gypsum and hydrated clay incorporated with polydimethylsiloxanes
Polypropylene, polybutylene
Metal carboxylic acid salts containing at least 6 carbon atoms
Calcium, barium and strontium compounds
Carboxylic acid salts, calcium stearate, barium stearate and strontium stearate, stearates, isostearates, oleates, palmitates, myristates, laurates, undecylenates, 2-ethylhexanoates, hexanoates
Salts of the following acids may be suitable: sulfinic, sulfonic, aromatic sulfenic, sulfamic, phosphinic and phosphoric acids
Polyolefins such as low density polyethylene and high density

-continued

polyethylene
Polypropylene, polybutylene
Copolymers such as polystyrene, polycarbonates
Polyesters, polyamides, polycaprolactams
Ionomers, polyurethanes, co- & ter-polymers
Acrylonitrile, butadiene, styrene, acrylic polymers, acetal resins, ethylene-vinyl acetate
Polymethylpentene
Polyphenylene oxide, polyphenylene oxide-polystyrene blends or copolymers with optional organic halides such as decabromodiphenyl oxide, dechlorane plus a chlorinated alicyclic hydrocarbon, and aluminum trihydrate

Flexibility Inducing Agents

Diglycidyl ether of linoleic acid dimer
Diglycidyl ether of polyethylene glycol
Diglycidyl ether of polypropylene glycol
Diglycidyl ether of alkylene oxide adduct of bisphenol A
Urethane prepolymer
Urethane modified epoxy resin
Polycarboxyl compounds
Polycaprolactone
Phenoxy resin

Flattening Agents

Amorphous Silica 1–2% by total resin weight, such as OK 411, produced by DeGussa, Inc. (Frankfurt, Germany), available through its pigment division in Teterboro, NJ
Silica
Micronized polyethylene

Grease Resistant Agents

Carboxymethylcellulose, methylcellulose, methylethylcellulose, hydroxypropylmethylcellulose, hydroxypropylcellulose

Hand Altering Agents

Protein structures made to imitate some borrowed property on or near the surface of the polymers.
Natural and synthetic beta-pleated sheet proteins
Hydrolized silk such as "Crosilk," a commercially hydrolized silk protein (Croda, Inc. New York, NY). Crosilk is a 10,000 molecular weight protein made by hydrolizing silk, and is comprised of 17 different amino acid segments, ranging in percent by weight of 0.1% to 20.3%.
Polyolefin fiber or fabric

Humidity Controlling Agents

Solid copper salts, preferably organic copper salts such as copper formate, copper acetate, copper oxalate and others.

Ion-Exchange Agents

Duolite C255H ™ by Diamond Shamrock
Ammonium salts
Chloride
Compounds and materials exhibiting acidic or basic functionality
Nitrate
Zeolite beta, zeolite chabazite (low calcium)

Light Fastness Inducing Agents

Ink dyes
Cationic dyes
Acid dyes
Monosulfonic acid, disulfonic acid, sulfonic acid-carboxylic acid

Light-Reflective Agents

Titanium oxide
Zinc oxide

Mildew Resistant Agents

Thiazolylbenzimidazole
Zinc phosphite
Derivatives of phenol
Derivatives of benzothiazole
Organosilicon quaternary ammonium salt

Processing Agents

Crosslinking inhibitors
Rheological agents
Hydrophilic polymers
Polyvinyl alcohol

Proteins

Silk protein
Fibroin
Collagen
Palladium

Radio Frequency Shielding Agents

Photoresistive films made of polyamide or SOG (Spun On Glass)
Magnetic films
Piezoelectric
Photoresistive films as a switchable EMI barrier

Rot Resistant Agents

Zinc chloride, chromated zinc chloride

Stain Resistant Agents

A mixture of phenyl vinyl ether/maleic diacid copolymer and 2-(4-hydroxy-methyl-phenoxy)-ethyl vinyl ether/maleic diacid copolymer and a copolymer obtained by the reaction of phenyl vinyl ether 2-(4-hydroxy-methyl-phenoxy)-ethyl vinyl ether and maleic anhydride
Erional ™ NBS, Intratex N ™
Mesitol, FX-369, CB-130, Nylofixan P

Therapeutic Agents

Antibiotics
Chemotherapeutic compounds
Hormones
Analgesics such as aspirin
Vitamins
Spermacides such as ricinleic acid, p-diisobutylphenoxypolyethoxyethanol, boric acid, and nonoxynol-9.
Drugs
Molecular sieves or other enclosed forms containing all of the above.

Thermal Conductive Agents

Aluminum particles such as aluminum nitride and alumina
Fillers such as silver
Graphite
Silicon carbide
Boron nitride
Diamond dust
Synthetic resin

Ultraviolet-Absorbing Agents

Benzophenone and its derivatives
Aryl group-substituted benzotriazole compound
Cinnamic acid esters
Benzoxazole
4-thiazolidone compounds
Titanium dioxide
Zinc oxide

Water Repellent Agents

Fluoroalkylsilane
Alkylsilane
Dimethylpolysiloxane
Flourine-type water repellent agent (Asahi Guard AG710)
Silazane compound, e.g., $(CH_3)_3SiNH—Si(CH_3)_3(6)$
Stearic acid salts
Zirconium compounds
Fluorosilicon type KP-801
Epoxy group-containing organosiloxanes
Polysiloxanes containing fluorine atoms
Perfluoroalkyl-silicone-KP801
Dimethylamino-silicone
Wax

Some additives and/or modifiers may or may not be combined with the thixotropic material prior to application in the porous substrate. These materials are applied to the surface of the porous substrate by depositing or metering, or by other like means.

Other additives and/or modifiers suitable for use in the practice of the present invention include compounds that contain reactive sites, compounds that facilitate the controlled release of agents into the surrounding environment, catalysts, compounds that promote adhesion between the treating materials and the substrate, and compounds that

alter the surface chemistry of articles produced from the treated substrates.

Reactive sites contemplated in the practice of the present invention include such functional groups as hydroxyl, carboxyl, carboxylic acid, amine groups, and the like, that promote physical and/or chemical interaction with other materials and compounds. For example, the modifier may be an enzyme or metal that catalyzes a specific reaction. Alternatively, the modifier may bind an agent. The phrase "capacity to bind," as used herein, refers to binding by both covalent and non-covalent means. Polyurethane is an example of a modifier with reactive sites that specifically bind iodine, the agent. A protein is an example of a modifier with reactive sites that specifically bind an antibody, the agent. The resulting articles are useful, for example, where iodine release is desirable (e.g., as a disinfectant), due to the tendency of iodine to sublime under ambient conditions.

The modifier or agent may also be a biologically active or "bioactive compound" such as an enzyme, antibody, antigen, or protein. For example, the modifier may be an antibody and the agent, a target protein, and the like. Or, the modifier may be a protein, and the agent, a target antibody. Such embodiments are particularly useful to the field of medical diagnostics.

Alternatively, the modifier may be capable of binding any proteinaceous material regardless of its bioactivity, such as polypeptides, enzymes or their active sites, as well as antibodies or antibody fragments. These embodiments, as contemplated in the practice of the present invention, are applicable to both research- and industrial-scale purification methods.

Depending on the end use of the treated material, a variety of modifiers containing reactive sites can be used. For example, modifiers can be employed that bind agents that are airborne organic contaminants. The particular compound employed as the modifier will depend on the chemical functionality of the target agent and could readily be deduced by one of skill in the art.

Also contemplated by the present invention is the use of modifiers that are capable of promoting the release of an agent from the treated web. For example, where the agent is being released from a thixotropic material that is hydrolytic, the modifier may be a hygroscopic compound such as a salt that promotes the uptake of water. As water is drawn into the material, the thixotropic material degrades by hydrolysis, thus releasing the agent. Alternatively, the modifier may promote the release of an agent from the treated web by creating pores once the resulting article is placed in a particular environment. For example, a water-soluble hygroscopic salt can be used to induce pore formation in thixotropic materials when placed in a humid or aqueous environment. Thus, dissolution of the salt promotes the release of the agent from the treated substrate. Other such modifiers that promote the release of an agent from materials are known to those of skill in the art. Agents suitable for use in these embodiments include therapeutic agents, biologically active agents, pesticides, biocides, iodine, and the like.

Also contemplated for use in the practice of the present invention as the modifier component are hydrogels. Hydrogels are polymeric materials that are capable of absorbing relatively large quantities of water. Examples of hydrogel forming compounds include polyacrylic acids, sodium carboxymethylcellulose, polyvinyl alcohol, polyvinyl pyrrolidine, gelatin, carrageenan and other polysaccharides, hydroxyethylenemethacrylic acid (HEMA), as well as derivatives thereof, and the like.

Control of the pressurized application step can be provided at a number of areas since the shear process is sensitive to the viscosity of the polymer composition both at atmospheric pressure and at superatmospheric pressure. The ambient temperature affecting the polymer as it is applied, and the pressure-induced temperature changes occurring during controlled placement of the polymer also play roles in viscosity and therefore the shear process. Of course, the chemical make-up of the polymer composition also plays a role in the shear process and assists in the formation of an internal layer and/or internal encapsulation of the fibers or structural elements of the web.

The amount of polymer utilized and the weight add-on thereof are again variable and dependent upon several things such as the treated web, the desired end use of the web, cost and the like. Web weight add-ons can be as little as about 1 to 5 weight percent up to about 200 weight percent of the untreated web. For producing breathable, water-repellent fabric webs of this invention, weight add-ons are preferably in the range of about 10 to about 100 weight percent of the weight of the untreated web.

The fluorochemical saturant composition may also contain a bonding agent. The bonding agent can facilitate the bonding of the water repellent chemical and/or the impregnate to the three-dimensional structure of the web within which it is saturated. Mobay Silopren™ bonding agent type LSR Z 3042 and Norsil 815 primer are representative compositions that can be used to facilitate bonding of the water repellent chemicals and/or impregnant to and within the web. Use of the bonding agents is not essential to the practice of this invention, but may improve bonding of the fluorochemical and/or the polymer composition to fibers.

The fluorochemical particularly, and also the bonding agents when used, are preferably affixed to the three-dimensional structure of the web prior to the controlled placement of polymer within the web. Complete affixing is not necessary for the fluorochemical. The fluorochemical will apparently facilitate the pressured application of a polymer composition even if the fluorochemical is not preliminarily fixed within or located within the web being treated. However, fixing, especially by sintering, appears to cause the water repellent chemicals to flow and to become better attached to the three-dimensional structure of the web. In this regard, a lesser amount of fluorochemical will remain in place better, and will better facilitate the subsequent pressured application of the polymer, if the sintering or insolubilizing step is performed prior to such a pressured application.

After fluorochemical saturation followed by controlled polymer placement and curing, a web may have a surface contact angle with the polymer of greater than about 70 degrees, and more typically greater than about 90 degrees. Web pressures can involve transverse force or pressure in the range of tens to thousands of pounds per square inch of web surface.

Similar to the functional qualifications achieved by the use of a fluorochemical in the preferred saturating pretreatment step, the polymer introduced by the pressured application step can be defined by its functional qualifications. For example, the silicone polymer produces a contact angle with a fluorochemical treated web of greater than about 70 degrees. The contact angle of a web with a fluorochemical will be within a range of about 90 degrees to about 180 degrees while the contact angle of a fluorochemically treated web with the silicone polymer will be within a range of about 70 degrees to about 180 degrees.

The contact angle exhibited by the silicone polymer can be, if desired, qualified against the particular web saturated with the particular fluorochemical saturant. The selection of

a suitable silicone polymer composition may be determined by the nature of the previously applied fluorochemical saturant. The fluorochemical saturant and silicone polymer compositions are, however, not critical to the practice of this invention since wide respective compositional ranges may be involved. In particular, a substantially undiluted liquid silicon rubber which is available from suppliers, such as GE, Dow Corning, and Mobay-Bayer, will characteristically form a contact angle of much greater than about 70 degrees, and typically greater than about 90 degrees, with typical porous webs (such as fabrics) that have a residue of fluorochemical upon (and within) the web resulting from a prior saturation.

The polymer composition can carry additives into the three-dimensional structure of the web in the pressured application steps of the method of the invention. Further, the polymer composition, when cured, is capable of adhering to structural elements, fibers, yarns, and the like, and any additives dispersed therein. Thus, additives are positioned adjacent to or on surfaces of structural elements, yarns, fibers and the like, in a position where they can be beneficial.

The energy can also be used to drive additives and/or modifiers to various selected positions within the porous web. During this stage, the viscosity of the thixotropic material becomes low enough and the application thickness thin enough such that additives and/or modifiers are able to move with either the sufficient mechanical energy or wave induced energy. Depending on the affinity of the additive and/or modifier for the thixotropic impregnant material as compared to the substrate/impregnant and impregnant/air interfaces, the additive and/or modifier will migrate to a particular region within the web. This migration is referred to herein as "surface blooming." The extent and rate of migration can be controlled by controlling the viscosity and thickness of the impregnant and the mobility of the particular additive and/or modifier. Both characteristics depend on the amount of energy provided to the system. Due to the nature of the thixotropic material, the additives and/or modifiers can be fixed at any location along their migratory path. For example, the amount of energy directed at the impregnant and web is decreased as the additives and/or modifiers migrate into the target positions. As the viscosity of the thixotropic impregnant rises, the additives and/or modifiers become essentially locked in place. This cycling of energy may be repeated in this stage, as well as in Stages 4 and 5, discussed below, until the additives and/or modifiers are finally moved and fixed into the preselected position.

Surface blooming is a term describing both the migration and exact orientation of the additive and/or modifier on or near the surface of the polymer. There seems to be either such a thin layer of the polymer (mono layer) or an actual breaking of the surface structure of the polymer so as to allow the exposure of the additive and/or modifier. It can also be applied to a time dependent effect whereby over time and exposure to movement and ambient conditions, the additive and/or modifier becomes exposed, as with time released agents.

The phenomenon referred to as "surface blooming" is believed to be the result of several factors working in conjunction, some of which are described above. The alternating silicon and oxygen (siloxane) bonds create a flexible backbone, and rotation is fairly free about the Si—O axis, especially with small substituents, e.g., methyl, on the silicon atoms. Rotation is also free about the Si—C axis in methylsilicon compounds. As a result of the freedom of motion, the intermolecular distances between methylsiloxane chains are greater than between hydrocarbons, and

intermolecular forces are smaller. Polydimethylsiloxane (PDMS) contains a very surface active group, —CH_3, whose activity is presented to best effect by the unique flexibility of the backbone. A more complete description of the surface characteristics of polydimethylsiloxanes is available in *The Surface Activity of Silicones: A Short Review*, Michael J. Owen, Ind. Eng. Chem. Prod. Res. Dev., v. 19, p97 (1980); and the *Encyclopedia of Polymer Science and Engineering 2d Ed.*, Wiley, N.Y., v. 15, Silicones (1985–90); all herein incorporated by reference.

Additional control over the positioning of additives and/or modifiers may be exerted during the curing process in Stage 8, discussed below. This control relates to another mechanism of additive and/or modifier movement during treatment as described in the discussion of Stage 8 below.

Energy sources contemplated for use in the practice of the present invention include subjecting the curable, thixotropic material and one or more modifiers to shearing conditions ("treating materials"). For example, the shearing conditions may be provided by passing the treating material and web in contact with one or more blades at a fixed orientation with respect to the blades. The blades may be either rigid or flexible to accommodate a greater variety of web materials. For example, a more rigid blade may be used if the web is soft and flexible. Similarly, a flexible blade may be used if the web is hard and rigid.

Alternatively, the energy may be provided by passing the treating materials and web through rollers at a controllable pressure. Other sources of energy contemplated for use in the practice of the present invention include thermal energy, ultrasonic energy, electron beam, microwave, and electromagnetic radiation.

Examples of additives that are dispersible in effective amounts in a viscous polymer composition (typically at a concentration of about 0.1 to 20 weight percent (based on total composition weight) include ultraviolet absorbers, flame retardants, aluminum hydroxide, filling agents, blood repellents, flattening agents, optical reflective agents, hand altering agents, biocompatible proteins, hydrolyzed silk, and the like. Hydrolyzed silk is a texturing agent that imparts a substantially silky feel to a fabric treated in accordance with the method of the invention regardless of whether or not such treated web or fabric is itself silk.

Examples of other polymer dispersible agents include those affecting thermal conductivity, radiation reflectivity, electrical conductivity, and other properties. For example, if a metallic sheen and/or thermal or electrical conductivity or infrared background blending is desired, powdered metals may be dispersed therein.

The pressured application of the polymer is sensitive to the viscosity of the polymer composition. Temperature affects the polymer composition by reducing or altering its viscosity. Shear-induced temperature changes occurring during application or during subsequent shear processing of the polymer can affect viscosity. The chemical composition of the polymer also plays a role in the treating process and effects in the treatment of web structural elements (including fibers) and the regulation of the filling of interstices and open cell voids.

Various machines and procedures can be used for performing the process of the invention. Illustrative machines and processes of use which are suitable for use in the practice of this invention, are described in U.S. application Ser. No. 08/407,191, filed Mar. 17, 1995 and hereby incorporated by reference. A preferred apparatus for carrying out the present invention is described below.

The apparatus employed in the present invention functions first to apply and preferably concurrently to shear thin

and place a polymer composition, with one or more additives and/or modifiers optionally mixed in the composition, into a web under pressure. Such polymer composition is then reintroduced, distributed, and metered in a controlled manner in the web with the aid of transversely applied shearing force and compressive force such that the polymer composition becomes distributed in the web so that additives and/or modifiers are oriented on and within the (a) thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) some combination of (a) and (b). During treatment, the web is longitudinally tensioned and the pressurized application and the subsequent shearing and compressive actions are successively accomplished in localized zones preferably extending generally laterally across the web (that is, generally perpendicularly to the direction of such longitudinal web tensioning) using transversely applied force exerted locally against surface portions of the web during each controlled placement and shearing operation. The web is conveniently and preferably, but not necessarily, moved longitudinally relative to such laterally extending web processing zones. In treating short lengths of a fabric, the blades may be moved relative to a stationary length of fabric. The pressurized application, shearing and compressing steps are preferably carried out successively or sequentially. Such zones are themselves preferably at stationary locations while the web is moved, but if desired, the web can be stationary while the zones are moved, or both. The result is that the polymer composition flows into the web and is distributed internally generally uniformly to a predeterminable and controllable extent.

Some additives and/or modifiers, due to their physical and chemical properties, cannot be incorporated on and/or within a web by pre-treating the web or by mixing the additives and/or modifiers into the polymer composition. Such additives and/or modifiers can be topically applied to the web after the pressured, shear thinning stage described above, but before curing. Once topically applied, the additives and/or modifiers are forced into the web by passing through the exit nip rolls. The additives and/or modifiers will adhere to the polymer composition that forms encapsulated fibers, an internal layer, or some combination of the above.

FIG. 5 depicts a schematic, side elevational view of a preferred apparatus for practicing the methods of the present invention. In this embodiment a continuous web 302 is moved under tension along a web pathway from a supply roll 301 to a take-up roll 327.

The primary tension is a result of the differential rate between the driven entrance pull stand designated as 306 and the driven exit pull stand designated as 322, whereby the exit pull stand 322 is driven at a rate faster than the entrance pull stand 306. Other controllable factors which effect tension are the diameters of blade rolls 309, 314, 316, 318; the vertical depth of blades 311, 315, 317; the durometer of the entrance pull stand rolls 304, 305 and rubber roll 321 of the exit pull stand, and the friction as the web passes under the blades. Blade roll 316 can optionally be a nip roll, as shown with the top roll 329. This allows for the creation of multiple tension zones to help shear thin the polymer composition and place one or more additives and/or modifiers on or within the web.

Web 302 passes between the nip of the two rolls 304 and 305 of the entry pull stand 306. The entry nip is adjustable to produce a force of from about 100 lbs. to about 5 tons on the web, passing between the two rolls. The weight of top roll 305 provides an even distribution of force throughout the web width. Web 302 is flattened at this point and the interstitial spaces are reduced laterally and longitudinally. Bottom roll 304 has micro-positioning capability to provide for gap adjustment and alignment. The top roll 305 composition is chosen based on the durometer of a urethane or rubber roll.

Web 302 continues to move along past idler roll 308 and blade roll 309 and forms an entry angle α and an exit angle β with blade 311. Blade 311 is illustratively shown in FIG. 4. In FIG. 4, dimensions A, B, C, D, and E are typically and exemplarily illustrated as, respectively, about 3½ inches, about 1½ inches, about 2 inches, about ½ inch, and about 3/16 inch. The narrow edge is preferably milled to a tolerance of about 1/10,000 inch continuously along the edge surface of each blade which is typically and illustratively about 38 inches long. Each of the corners of the narrow edge is preferably and illustratively a hard (not beveled or ground) angular edge. Preferably, the combination of the leading edge condition and the two surfaces (the front and the bottom) that meet at the leading edge are RMS 8 or better in grind and/or polish. For purposes of the apparatus of FIG. 5, the blade in FIG. 4 has a leading edge 250 and a trailing edge 260. Entry angle α can be varied by adjusting: (a) the height and diameter of blade rolls 309 and 314, (b) the horizontal position of blade rolls 309 and 314, (c) the angle of blade 311, and (d) the height of blade 311. Similarly, the entry and exit angles of blades 315 and 317, can be varied by adjusting the same devices surrounding each blade.

For illustrative purposes, increasing the height and diameter of blade roll 309 decreases entry angle α. Rotating blade 311 clockwise, with web 302 running left to right, increases entry angle α. Likewise, rotating blade 311 counterclockwise, with web 302 running left to right, decreases entry angle α. Decreasing the distance between blade roll 309 and blade 311 decreases entry angle α. Increasing the downward depth of blade 311 into web 302 decreases entry angle α.

The angle of blades 311, 315, and 317 are completely changeable and fully rotational to 360°. The fully rotational axis provides an opportunity for more than one blade per rotational axis. Therefore, a second blade having a different thickness, bevel, shape, resonance, texture, or material can be mounted. Ideally the apparatus contains two or three blades per blade mount. The blade mounts are not shown.

The force or pressure of blade 311 applied against web 302 is determined by the vertical positioning of blade 311 in the blade mount. The greater the downward depth of blade 311, the greater the force or pressure. Blade pressure against the web is also accomplished through the tension of the web as described above.

The same line components that affect entry angle α, also affect exit angle β. Any changes in the height, diameter, or horizontal positioning of blade rolls 309 and 314, affects exit angle β. If the angle of blade 311 is rotated clockwise as described above, entry angle α increases, thus decreasing exit angle β.

As web 302 moves from left to right in FIG. 5, polymer, optionally mixed with one or more additives and/or modifiers, is deposited on web 302 with polymer applicator or dispersion means 310. Polymer applicator 310 can be a pump, a hose, or any available application device for applying polymer onto the surface of the web. Polymer applicator 310 is located directly in front of blade 311. The polymer is immediately shear thinned, placed into, and extracted from web 302 by the leading edge of blade 311, thus controlling the amount of polymer remaining in web 302. The bevel of blade 311 can effect entry angle α and the sharpness of the leading edge of blade 311. A sharper leading edge has a

greater ability to push the weave or structural elements of web 302 longitudinally and traversely, increasing the size of the interstitial spaces. As the web passes the leading edge of blade 311, the interstitial spaces snap back or contract to their original size.

As web 302 moves from left to right in FIG. 5, the process of shear thinning and placing polymer into and extracting it out of web 302 is repeated at subsequent blades 315 and 317, thus controllably placing the polymer throughout web 302. Web 302 then passes over idler roll 319 and additives and/or modifiers are topically applied to web 302 by additive applicator or dispersion means 328. Additive applicator 328 can be a pump, or hose, or any application device for applying additives onto the surface of the web. Additive applicator 328 is located directly in front of the exit pull stand 322.

Web 302 then passes between driven exit pull stand 322 which consists of rolls 320 and 321. Pull roll 320 is a driven roll proportionally driven at a predetermined rate slower than entry roll 304. Pull roll 321 does not apply pressure so much as it achieves a high degree of surface area in which web 302 must come into contact with. The larger the surface area, the higher the degree of contact friction. Pull roll 321 can be adjusted to have sufficient downward force to eliminate any slippage between web 302 and pull roll 320.

After web 302 passes from exit stand 322, it then moves into an oven 323 for curing. Rolls 324, 325, and 326 provide a tension regulating means and also serve to provide a cooling pathway for web 302 as it emerges from oven 323 before passing onto take-up roll 327.

The cure temperature of oven 323 is thermostatically controlled to a predetermined temperature for web 302 and the polymers used. Machine runs of new webs are first tested with hand pulls to determine adhesion, cure temperature, potentials of performance values, drapability, aesthetics, etc. The effect on web 302 depends on the temperature of oven 323, dwell time and curing rate of the polymer. Web 302 may expand slightly from the heat.

Oven 323 functions to cure the polymer composition that is controllably placed into web 302. Oven 323 can be operated with gas or other energy sources. Furthermore, oven 323 could utilize radiant heat, induction heat, convection, microwave energy or other suitable means for effecting a cure. Oven 323 can extend from about 12 to 20 yards, with 15 yards long being convenient.

Curing temperatures from about 320° F. to about 500° F., applied for times of from about two minutes to about thirty seconds (depending on the temperature and the polymer composition) are desirable. If a curing accelerator is present in the polymer, curing temperatures can be dropped down to temperatures of about 265° F. or even lower (with times remaining in the range indicated).

The cure temperature of oven 323 and the source and type of cure energy, are controlled for a number of reasons. The cure temperature of oven 323 is controlled to achieve the desired crosslinked state; either partial or full. The source and type of energy can also affect the placement of the polymer and additives. In place of an oven, or in combination with an oven, a source of radiation can be employed (electron beams, ultraviolet light, or the like) to accomplish curing, if desired. For example, by using a high degree of specific infrared and some convection heat energy for cure, some additives can be staged to migrate and/or bloom to the polymer surfaces.

Oven cure dwell time is the duration of time the web is in oven 323. Oven cure dwell time is determined by the speed of the oven's conveyor and physical length of the oven. If the dwell time and temperature for a particular web is at maximum, then the oven conveyor speed would dictate the speed of the entire process line or the length of the oven would have to be extended in order to increase the dwell time to assure proper final curing of the web.

Take-up roll 327 is operated at approximately the same speed as supply roll 301. When the rotational speeds of take-up roll 327 are not synchronized with rotational speeds of supply roll 301, the tension roll combination of rolls 324, 325, and 326 can be used to reduce web slack.

Web speed is proportional to the variable speed of the motor which drives entrance pull stand 306 and exit pull stand 322. Web speed can effect the physics of the polymers as web 302 passes under blades 311, 315, and 317. Web transport speeds can vary widely; for example, from about two yards per minute to about ninety yards per minute.

FIG. 1 illustrates the phenomenon referred to herein as "thixotropic looping." This figure represents the viscosity changes of a polymer composition applied to a web by the apparatus shown in FIG. 5. For the purposes of demonstrating the general phenomenon, each blade is the same size and shape and each blade is positioned the same so that the shear rate at each blade is identical.

As the polymer composition comes in contact with the first blade, the shear stress reduces the viscosity of the polymer composition. Immediately after the first blade, the polymer begins to increase in viscosity, but never returns to its initial viscosity. As it comes in contact with the second blade, again the viscosity drops, but not as severe as with the first blade. Immediately after the second blade, the viscosity increases, but not to its initial viscosity. This phenomenon occurs again at the next blade and would continue at subsequent blades until the polymer reached its minimum viscosity.

A general process for making a porous web of this invention comprises the steps of: optionally pre-treating a flexible, porous web with a modifier by saturation methods known in the art; tensioning a flexible, porous web as above characterized; optionally mixing one or more additives and/or modifiers with a curable shear thinnable polymer composition; applying the mixed curable shear thinnable polymer composition, described above, to at least one web surface; and then moving over and against one surface of the tensioned web a uniformly applied localized shear force to: shear thin the optionally mixed polymer composition, uniformly place the composition within the web, at least partially individually encapsulate or envelop surface portions of at least some of said fibers through the web matrix or position said composition in a desired web internal region or some combination of both. Some additives and/or modifiers can then optionally be topically applied and pressed onto and into the web by the exit pull stand. Thereafter, the web is subjected to conditions sufficient to cure the composition in said web. Curing is accomplished by heat, by radiation, or both.

A presently preferred process for making a fluorochemical and silicone resin treated web having breathability, water resistance, rewashability, and one or more additives and/or modifiers, which is adapted for continuous operation comprises the successive steps of: impregnating the web with a fluorochemical, longitudinally tensioning the fluorochemical impregnated web while sequentially first applying to one surface thereof a curable silicone polymer composition with one or more additives and/or modifiers therein and concurrently applying a transversely exerted localized compressive force against said surface, and moving over said surface of the web substantially rigid shearing means which exerts

transversely an applied, localized shear force against said surface to shear thin the polymer and wipe away exposed portions of silicone polymer composition on said surface, thereby forming an internal layer of silicone polymer and/or enveloping at least of the fibers or passageways through the matrix, or both; optionally topically applying one or more additives and/or modifiers; and curing the silicone polymer composition in the web.

The additives and/or modifiers may also be selectively positioned during the final stage of the treatment process. When a diluent is incorporated into the polymer composition, the additives and/or modifiers may be moved by controlling the volatization of the diluent. As the diluent is driven to the air/polymer surface by heat, it carries the additives and/or modifiers with it to the surface. As the polymer composition cures, its viscosity increases thus fixing the additives and/or modifiers in position. Appropriate diluents include water and low molecular weight silicones and solvents such as aromatic solvents (e.g., toluene), low molecular weight ketones (e.g., acetone, methyl ethyl ketone, and the like. Positioning of the additive and/or modifier in this manner can be controlled by controlling among other variables, the amount of energy directed at the treating materials and substrate and the amount and type of diluent in the polymer composition. Positioning of additives and/or modifiers can also occur by the pressured application of additives and/or modifiers onto and into the web. Just prior to passing the treated web through the exit nip rolls, one or more additives and/or modifiers can be topically applied to the web, thereby forcing the additive(s) and/or modifier(s) onto and into one or more surfaces of the web. The additive and/or modifier can adhere to the web and/or the polymer composition in the web. Preferably the additive (s) and/or modifier(s) adheres to the polymer composition that encapsulates the individual fibers or filaments, that forms an internal layer, that fills some of the interstitial spaces of the web, or that produces some combination of the foregoing.

The following text concerns the theory of the invention as it is now understood; however, there is no intent herein to be bound by such theory.

The presently preferred polymer composition used in the treatment of webs by this invention is a non-Newtonian liquid exhibiting thixotropic, pseudoplastic behavior. Such a liquid is temporarily lowered in viscosity by high pressure shear forces.

One aspect of the invention is a recognition that when high forces or sufficient energy are applied to curable polymer compositions, the viscosities of these materials can be greatly reduced. When the viscosity is repeatedly reduced, the result is one of thixotropically looping or massaging the viscosity rheology crosslink opportunities and overall orientation of one or more additives and/or modifiers on and/or within the (a) thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) some combination of (a) and (b). Thixotropic looping is illustratively and qualitatively shown in FIG. 1, for an apparatus containing three blades. Conversely, when subjected to curing, the same liquid composition sets to a solid form which can have a consistency comparable to that of a hard elastomeric rubber. The internal and external rheological control of polymer materials achieved by the present invention is believed to be of an extreme level, even for thixotropics. When subjected to shear force, the polymer composition is shear thinned and can flow more readily, perhaps comparably, for illustrative purposes, to water.

The invention preferably employs a combination of: (i) mechanical pressure to shear thin and place a polymer composition into a porous web; (ii) an optional porous web pretreatment with a water repellent chemical, such as a fluorochemical, which is theorized to reduce the surface tension characteristics of the web and create a favorable surface contact angle between the polymer composition and the treated web which subsequently allows, under pressure and shear force exerted upon an applied polymer composition, the production and creation of an internal coating or layer which envelopes fibers or lines cell walls in a localized region within the web as a result of polymer flow in the web or which encapsulates the fibers within the web; and (iii) a polymer composition impregnant preferably having favorable Theological and viscosity properties which responds to such working pressures and forces, and is controllably placed into, and distributed in a web. This combination produces a web having the capability for a high degree of performance. This product is achieved through pressure controlled placement and applied shear forces brought to bear upon a web so as to cause controlled movement and flow of a polymer composition and one or more additives and/or modifiers into and through a web. Preferably, repeated compressive applications of pressure or successive applications of localized shear forces upon the polymer in the web are employed.

By the preferred use of such combination, a relationship is established between the respective surface tensions of the polymer and the web, creating a specific contact angle. The polymer responds to a water repellent fluorochemical pretreatment of the substrate so as to permit enhanced flow characteristics of the polymer into the web. However, the boundary or edge of the polymer is moved, preferably repeatedly, in response to applied suitable forces into the interior region of a porous web so as to cause thin films of the polymer to develop on the fiber surfaces and to be placed where desired in the web.

Thixotropic behavior is preferably built into a polymer used in the invention by either polymer selection or design or additive/filler design. For example, it now appears that thixotropic behavior can be accentuated by introducing into a polymer composition certain additives that are believed to impart enhanced thixotropy to the resulting composition. A lower viscosity at high shear rates (during application to a web) is believed to facilitate polymer flow and application to a web, whereas a polymer with high viscosity, or applied at a low shear rate (before and/or after application) actually may retard or prevent structural element (including fiber) envelopment or encapsulation.

Illustratively, the practice of this invention can be considered to occur in stages:

In stage 1, a silicone polymer composition impregnant is prepared. It can be purchased commercially and comes in typically two parts designated as A and B. For example, in a silicone polymer composition, as taught in U.S. Pat. No. 4,472,470, a base vinyl terminated polysiloxane is the A part, while a liquid organohydrogensiloxane controlled crosslinking agent is the B part. Certain remaining components, such as a resinous organopolysiloxane copolymer and a platinum catalyst may (or can) apparently initially be in either part A or part B.

Stage 2 can be considered to involve the mixing of such a product's parts with or without additives. Changes in viscosity can be obtained and measured based on applied shear rates and shear stresses. Such changes can be experienced by a polymer with or without additives.

Up to a 99% reduction in viscosity of a liquid silicone polymer composition is believed to be obtainable by the shear forces involved in the shear thinning and forcing of a silicone polymer composition impregnant into a web and almost simultaneously extracting the correct amounts out. Thereafter, a very substantial increase in polymer viscosity is believed to be obtainable taking into account these same factors. Normally, the most significant factor is now believed to be the shear gradient that typically reduces the viscosity of the polymer below the starting or rest viscosity.

Stage 3 can be considered to be the pressure introduction stage. Up to a 99% reduction of the polymer viscosity is believed to be obtainable due to the applied shear forces, elapsed time, temperature, radiation and/or chemical changes. Thereafter, a significant increase or even more in the resulting polymer viscosity is believed to be obtainable. In this stage, partial curing of the polymer may take place. Most commonly, polymer viscosity is substantially decreased during the pressure controlled placement Stage 3 by the application of shear forces.

Stage 4 can be considered to be the first stage internal matrix dispersing and reintroduction with metering, and also recovery and recycle of excess polymer. Typically, within this Stage 4, the shear forces cause a substantial but temporary lowering of polymer viscosity, causing it to flow upon and into the three-dimensional structure of the web. The initial viscoelastic character of the polymer is typically theorized to be recovered almost immediately after shear forces are removed.

Stage 5 can be considered to be a second stage internal matrix dispersing and reintroduction with metering and also recovery and recycling of excess polymer. The variations in the viscosity of the polymer are equivalent to Stage 4. The viscosity of the polymer is again lowered causing it to flow within the web. Because of the application of repeated shear force induced reductions in viscosity, the thixotropic behavior of a polymer may not undergo complete recovery, following each application of shear force and the viscosity of the polymer may not revert to its original placement values. The polymer composition is believed to have the capacity to form enveloping internal coating in a predetermined region wherein the interstices or open cells are substantially completely filled within the three-dimensional matrix constituting a web during the time intervals that the is caused to flow under pressure in and about matrix components. In between these times, the polymer may recover substantially all of its initial high viscosity, although perhaps slightly less so with each repeated application of shearing pressure or force.

Stage 6 can be considered the optional application of additives and/or modifiers. Some additives and/or modifiers, due to their physical and chemical properties, cannot be incorporated on and within a web by pre-treating the web or by mixing the additives and/or modifiers into the polymer composition. Such additives and/or modifiers can be topically applied to the web after the pressured, shear thinning stage described above, but before curing. Once topically applied, the additives and/or modifiers are forced into the web by passing through the exit nip rolls. The additives and/or modifier can adhere to the polymer composition or to the individual fibers of the web. Preferably, the additives and/or modifiers will adhere to the polymer composition that fills the warp filled interstitial spaces, forms encapsulated fibers, an internal layer, or some combination of the above.

Stage 7 can be considered to be occurring just as curing is begun, and just as heat or other radiation is introduced.

Stage 8 can be considered to be occurring with regard to the exertion of control of curing. Typically, at least a partial curing (including controlled cross-linking and/or polymerizing) is obtained by relatively low temperatures applied for relatively short times. For example, when light cotton, nylon, or similar fabrics are being treated, temperatures under about 350°, applied for under about 10 seconds, result in partial curing.

In one embodiment of the present invention, the curable, thixotropic material plus additives and/or modifiers form a porous film having an average pore size in the range of 0 to 10 microns (although not zero microns). Porous films are produced by the addition of pore-forming agents to the thixotropic material. Examples of pore-forming agents include low molecular weight polymers and oligomers that can be subsequently washed from the treated substrate using appropriate solvents and co-solvents that are known by those skilled in the art.

In preferred embodiments of the present invention, sufficient energy is used to selectively position the additives and/or modifiers at specific locations within the porous web. As employed herein, the phrase "selectively positioned" refers to the localization of additive and/or modifier materials at desired regions within the porous web. "Selective positioning" is achieved by controlling a phenomenon unique to thin films known as "migratory surface bloom." Migratory surface bloom refers to the ability of an additive and/or modifier to migrate to the surface and assume its multi-dimensional conformation.

The phenomena referred to as "surface blooming" is believed to be the result of several factors working in conjunction, such as the size and shape of the additive(s) and/or modifier(s), the thickness of the thin film, and the characteristics of polydimethylsiloxanes. The alternating silicon and oxygen (siloxane) bonds create a flexible backbone, and rotation is fairly free about the Si—O axis, especially with small substituents, e.g., methyl, on the silicon atoms. Rotation is also free about the Si—C axis in methylsilicon compounds. As a result of the freedom of motion, the intermolecular distances between methylsiloxane chains are greater than between hydrocarbons, and intermolecular forces are smaller. Polydimethylsiloxane (PDMS) contains a very surface active group, —CH_3, whose activity is presented to best effect by the unique flexibility of the backbone. A more complete description of the surface characteristics of polydimethylsiloxanes is available in *The Surface Activity of Silicones: A Short Review*, Michael J. Owen, Ind. Eng. Chem. Prod. Res. Dev., v. 19, p97 (1980); and the *Encyclopedia of Polymer Science and Engineering*, v. 15, Silicones, (Wiley 1987); all incorporated herein by reference. In the present invention, the extent of surface bloom is controlled by controlling the amount of energy directed at the treating materials and web.

In one embodiment of the present invention, the additive and/or modifier is selectively positioned substantially on the application surface of the porous web. In another embodiment of the present invention, the additive and/or modifier is selectively positioned substantially on the surface opposing the application surface of the porous web. Alternatively, where the porous web is derived from discrete elements such as fibers that are encapsulated, the additive and/or modifier

can be selectively positioned substantially within the encapsulated material.

FIG. 2 is a schematic vector diagram illustrating the surface tension forces acting at the vertex boundary line of a liquid contact angle on a planar solid surface. It illustrates how surface tension forces might be measured between a silicone polymer composition and a fiber of a web (or a fabric) as treated by the invention.

For the purposes of the present invention, the term "surface tension" can be considered to have reference to a single factor consisting of such variables as intermolecular, or secondary, bonding forces, such as permanent dipole forces, induced forces, dispersion or nonpolar van der Waals forces, and hydrogen bonding forces. The strong primary bonding forces at an interface due to a chemical reaction are theorized to be excluded from surface tension effects; however, it is noted that even a small degree of chemical reactivity can have a tremendous influence on wetting effects and behavior affected by surface tension.

The unique feature of poly-dimethylsiloxanes is their high surface activity. Pure poly-dimethylsiloxanes typically exhibit surface tension values of 21 dynes/cm, which is higher than only fluorocarbons. The prevailing explanation for this phenomenon is the dense packing of methyl groups at the surface of the poly-dimethylysiloxanes. The low surface tension of poly-dimethylsiloxanes gives them surface-active properties both in aqueous and organic solutions. This phenomenon is further described in David T. Floyd's article: *Organo-Modified Silicone Copolymers for Cosmetic Use*, Cosmetic and Pharmaceutical Applications of Polymers, p. 49–72, Plenum Press (New York 1991), herein incorporated by reference.

Surface tension is believed to induce wetting effects which can influence the behavior of a polymer composition impregnant relative to the formation of either a fiber enveloped layer therewith in a fibrous porous web, fiber encapsulation or both. For example, adhesion is theorized to be a wetting effect. Spontaneous adhesion always occurs for contact angles less than about 90°. However, for a combination of a rough surface and a contact angle over 90°, adhesion may or may not occur. In fact, roughness becomes antagonistic to adhesion, and adhesion becomes less probable as roughness increases.

Also, penetration is theorized to be a wetting effect. Spontaneous penetration occurs for contact angles less than about 90°, and does not occur for contact angles over about 90°. The roughness of a solid surface accentuates either the penetration or the repellency action, but has no influence on which type of wetting takes place.

In addition, spreading is theorized to be a wetting effect. Retraction occurs for contact angles over 90° or over planar surfaces for any contact angle. However, spontaneous spreading for contact angles less than 90°, especially for small contact angles, may be induced by surface roughness.

FIG. 3 is a graph relating the contact angle over a smooth solid surface as a function of θ and i that apply respectively, to adhesion (I cos θ+1), penetration (i cos θ), and spreading (i cos θ−1).

Regions of adhesion versus abhesion, penetration versus repellency, and spreading versus retraction are shown by shaded areas. FIG. 3 illustrates what is theorized to be the relationship of a silicone polymer composition to silicone polymer composition solids in a treated web as regards such factors as adhesion, penetration, spreading, and retraction.

For purposes of this invention, the term "wetting" is used to designate such processes as adhesion, penetration, spreading, and cohesion. If wetting transpires as a spontaneous process, then adhesion and penetration are assured when the solid surface tension exceeds the liquid surface tension. Surface roughness promotes these spontaneous wetting actions. On the other hand, no such generalizations can be made when the solid surface tension is less than the liquid surface tension.

Surface tension is measured by S.T.L. units for liquid and by S.T.S. units for solids; both units are dyne/centimeter. When S.T.S. is less than S.T.L., then wetting is less ubiquitous and prediction of wetting behavior is more difficult. However, by taking advantage of the liquid/solid contact angle that forms when a liquid retracts over a solid, it is possible to calculate with reasonable accuracy the wetting behavior that can be expected. The reduction in liquid surface area can be computed in terms of the contact angle that the liquid makes with the solid surface. Contact angles are always measured in the liquid phase. There is a point of equilibrium where the surface tension forces become balanced.

By measuring the contact angle of a liquid on a solid, the wetting behavior of the liquid polymer composition can be measured.

This invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof, which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention and/or the scope of the appended claims.

EXAMPLES

Example 1

Liquid Silicone Polymer Preparation

100 parts by weight of the curable liquid silicone polymer available commercially from Mobay as "Silopren® LSR 2530" was mixed in a 1:1 ratio, as recommended by the manufacturer. A Hockmeyer F dispersion blade at low torque and high shear was used to do the mixing. To this mixture were added 5 parts by weight of BSF "Uvinul 400" and 5/10 parts by weight Dow Corning 7127 accelerator, believed to be a polysiloxane but containing an undisclosed active accelerated ingredient.

Examples 2–19

Liquid Silicone Polymer Preparation with One or More Modifiers

The procedure of Example 1 was repeated with various other commercially available curable viscous liquid silicone polymer compositions. To this product system a substituted benzophenone and other additives are optionally added, the results of which are shown in Table III. These examples illustrate that more than one additive can be combined in the practice of this invention. All parts are by weight.